Cambridge
Physical Series

Theory of Solution

LIBRARY
OF THE
UNIVERSITY OF CALIFORNIA.

Class

CAMBRIDGE PHYSICAL SERIES.

GENERAL EDITORS:—F. H. NEVILLE, M.A., F.R.S.
AND W. C. D. WHETHAM, M.A., F.R.S.

A TREATISE
ON THE
THEORY OF SOLUTION

London: C. J. CLAY AND SONS,
CAMBRIDGE UNIVERSITY PRESS WAREHOUSE,
AVE MARIA LANE,

AND

H. K. LEWIS,
136, GOWER STREET, W.C.

Glasgow: 50, WELLINGTON STREET.
Leipzig: F. A. BROCKHAUS.
New York: THE MACMILLAN COMPANY.
Bombay and Calcutta: MACMILLAN AND CO., LTD.

[*All Rights reserved.*]

A TREATISE

ON THE

THEORY OF SOLUTION

INCLUDING THE PHENOMENA OF

ELECTROLYSIS

BY

WILLIAM CECIL DAMPIER WHETHAM, M.A., F.R.S.
FELLOW OF TRINITY COLLEGE, CAMBRIDGE

CAMBRIDGE:
AT THE UNIVERSITY PRESS.
1902

QB54
W52

GENERAL

Cambridge:
PRINTED BY J. AND C. F. CLAY,
AT THE UNIVERSITY PRESS.

PREFACE.

THIS book was at first intended as the second edition of a small volume on *Solution and Electrolysis* published in the year 1895. It was, however, soon found necessary to rewrite such large portions of the text, and to incorporate so much fresh matter, that the result is in effect a new work.

Our knowledge of the phenomena of solution is growing rapidly, and as yet there is considerable difficulty in producing a systematic treatise. Moreover, the use of modern thermodynamic methods, founded on the investigations of Willard Gibbs, is extending to almost all branches of the subject, while such methods are still unfamiliar to many students of physics and chemistry. An introductory chapter has therefore been prefixed, explaining the thermodynamic principles which are applied in the body of the work.

Besides the papers of Willard Gibbs, the following books should be especially mentioned among those to which the writer is indebted: Buckingham's *Theory of Thermodynamics*, Roozeboom's *Heterogenen Gleichgewicht*, Bancroft's *Phase Rule*, Larmor's *Æther and Matter*, Duhem's *Mécanique Chimique*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Nernst's *Theoretische Chemie*, the works on Physical Chemistry of van 't Hoff, Lehfeldt, and J. Walker, van 't Hoff's *Chemical Dynamics*, Le Blanc's *Electrochemistry*, and *Das Leitvermögen der Elektrolyte* by Kohlrausch and Holborn. In these books the reader will find further details on particular points, while most of the new work on the subject can be studied, either in full or in abstract, in the pages of the *Zeitschrift für Physikalische*

130125

Chemie, the *Journal of Physical Chemistry* or the *Zeitschrift für Elektrochemie.*

Much that is of value in this book must be attributed to the kindly help of many friends. Notes and corrections of the older work referred to were sent by Professors J. H. Poynting, L. R. Wilberforce, and W. McF. Orr, while the wise and suggestive criticism of the late Professor G. F. FitzGerald added another to the many kindnesses for which the writer will always gratefully cherish his memory. Mr F. H. Neville read the earlier part of the manuscript of the new book, and gave useful information and advice; help on particular points was sought from the Earl of Berkeley, Professor J. J. Thomson, Dr J. N. Langley, Principal E. H. Griffiths, Mr S. Skinner and Mr G. F. C. Searle, while Professor Poynting read and criticized the chapters on osmotic pressure and allied phenomena. To all the writer offers his cordial thanks. Especially would he express his sincere gratitude and deep sense of obligation to Mr J. Larmor, whose kindness in reading some of the manuscript and all the proof sheets it is impossible adequately to acknowledge. Mr Larmor's wide knowledge and deep insight have enabled the writer to gain clear ideas on many points which before were doubtful, and the ungrudging way in which he has given time and trouble to this work has removed many blemishes which would otherwise have appeared therein. Finally the writer's thanks are due to his wife for preparing the index and for constant correction both of the manuscript and of the proof sheets which have developed into the following pages.

Trinity College, Cambridge.
December, 1902.

CONTENTS.

CHAP. PAGE

I. THERMODYNAMICS 1

Experimental basis of Thermodynamics. The first law. The second law. Work and energy. Complete cycles. Reversible processes. Reversible engines. The absolute scale of temperature. Generalized co-ordinates. Internal energy. Entropy. Thermodynamic potential. Conditions of equilibrium. Application of thermodynamic potential. Free energy. Application of the free energy principle.

II. THE PHASE RULE 32

Equilibrium. Equilibrium of phases. The phase rule. Non-variant systems. Monovariant systems. Divariant systems. Other systems. The principle of latent heat. Application of the phase rule. One component. Labile equilibrium. Allotropic solids.

III. THE PHASE RULE. TWO COMPONENTS. SOLUTIONS . 48

Compounds, mixtures and solutions. Anhydrous solutes. Hydrated solids. Concentration curves. Two liquid components. Alloys. Solid solutions. Two volatile components. Three components. The problems of solution.

IV. SOLUBILITY 78

General problem of solubility. Supersaturation. Solubility of gases in solids. Solubility of gases in liquids. Henry's law. Solubility of gases in salt solutions. Solubility of liquids in liquids. Solubility of solids in liquids. Influence of pressure on the solubility of solids. Solubility of mixtures. Solubility in mixed liquids. Tables of solubility.

CHAP. PAGE

V. Osmotic Pressure 95

Semi-permeable membranes. Osmotic pressure and vapour pressure. Perfect semi-permeable membranes. Theoretical laws of osmotic pressure. Osmotic pressure and heat of solution. Experimental measurements of osmotic pressure.

VI. Vapour Pressures and Freezing Points . . 122

Connection with osmotic pressure. The latent heat equation. The depression of the freezing point. Vapour pressures of concentrated solutions. Solubility of gases in liquids. Experimental measurements of vapour pressures. Boiling points. Determination of molecular weights. Freezing points. Osmotic pressure and freezing points of concentrated solutions. Experiments on the freezing points of solutions. Determination of molecular weights. Freezing points of alloys. Experiments on concentrated solutions.

VII. Theories of Solution 165

Thermodynamics as a basis for physical science. Application to the case of solution. Theory of direct molecular bombardment. Theory of chemical combination. Conclusion.

VIII. Electrolysis 176

Introduction. Volta's pile. Early experiments. Faraday's work. Polarization. Faraday's laws. Electrochemical equivalents. The electrolysis of gases. Nature of the ions.

IX. Conductivity of Electrolytes 197

Ohm's law. Experimental methods. Experimental results. Consequences of Ohm's law. Migration of the ions and transport numbers. Mobility of the ions. Experimental measurements of ionic velocity. Influence of concentration. Complex ions. Connexion between the mobility of an ion and its chemical constitution. Conductivity of liquid films.

X. Galvanic Cells 232

Introduction. Reversible cells. Electromotive force. Effect of pressure. Concentration cells. Different concentrations of the electrodes. Different concentrations of the solutions. Concentration double cells. Effect of low concentrations. Chemical cells. Oxidation and reduction cells. Transition cells. Irreversible cells. Secondary cells or accumulators.

CHAP. PAGE

XI. Contact Electricity and Polarization . . . 267

Volta's contact effect. Thermo-electricity. The theory of electrons. Single potential differences at the junctions of metals with electrolytes. Dropping electrodes. Electrocapillary phenomena. The theory of von Helmholtz. Electric endosmose. Single potential differences (continued). Electrolytic solution-pressure. Electrochemical series. Polarization. Decomposition voltage. Polarization at each electrode. Evolution of gases. Electrolytic separations.

XII. The Theory of Electrolytic Dissociation . . 312

Introduction. Osmotic pressure of electrolytes. Additive properties of electrolytic solutions. Dissociation and chemical activity. The mass law. Equilibrium between electrolytes. Thermal properties of electrolytes. Heat of ionization. Dissociation of water. The function of the solvent. Hydrolysis. Conclusion.

XIII. Diffusion in Solutions 369

Theory of diffusion. Experiments on diffusion. Diffusion and osmotic pressure. Diffusion of electrolytes. Potential differences between electrolytes. Liquid cells. Complete theory of ionic migration. Electrolytic solution pressure. Diffusion through membranes.

XIV. Solutions of Colloids 391

The colloidal state. Process of gelation and structure of gels. Coagulative power of electrolytes. The nature of colloidal solutions.

Additions 403

Table of Electrochemical Properties of Aqueous Solutions 407

Index 476

CORRECTIONS.

Page 12, line 8, read: But consequences of the second law of thermodynamics which only hold for reversible systems have sometimes been applied, etc.

Page 26, footnote, read: *Zeits. phys. Chem.* xi. 289 (1893).

Page 117, footnote 3, read: *Zeits. phys. Chem.* i. 481 (1887).

Page 122, add to heading of chapter: Freezing points of alloys. Experiments on concentrated solutions.

Page 162, the equation should be numbered (35).

Page 193, line 19, read: $0{\cdot}404 \times 10^{-11}$.

Page 197, add to heading of chapter: Conductivity of liquid films.

Page 206, the equation should be numbered (36).

Page 231, add to footnote: Patterson, *Phil. Mag.* Dec. 1902.

Page 241, line 18, read: to all kinds of reversible cells, etc.

Page 248, line 18, in the denominator of the expression for E, 96440 should be 9644, the ionic charge being here measured in c.g.s. units and not in coulombs.

Page 272, line 15, read: Let us imagine a circuit composed of two wires of different metals surrounded by a dielectric, the two metallic junctions being maintained at different temperatures. In applying, etc.

Page 328, the Figure should be numbered 64.

LIBRARY OF THE UNIVERSITY OF CALIFORNIA

CHAPTER I.

THERMODYNAMICS.

Experimental basis of thermodynamics. The first law. The second law. Work and energy. Complete cycles. Reversible processes. Reversible engines. The absolute scale of temperature. Generalized co-ordinates. Internal energy. Entropy. Thermodynamic potential. Conditions of equilibrium. Application of thermodynamic potential. Free energy. Application of the free energy principle.

Experimental basis of thermodynamics. The first law.

THE subject of thermodynamics, which deals with the relations between heat and the other forms of energy possessed by material systems, rests ultimately, like all physical sciences, on a basis of observation and experiment.

Careful measurements by Joule, Rowland, Griffiths and others have shown that, when various forms of mechanical and electrical energy are completely converted into heat by friction and similar processes, the quantity of heat produced by a given amount of work is always the same in whatever form and by whatever means the work is applied. Heat is thus a form of energy, and one thermal unit must have its definite mechanical equivalent in other forms of energy. This experimental generalization is one case of the principle of the conservation of energy, and constitutes the first law of thermodynamics.

The best modern determinations show that the amount of heat necessary to raise one gram of water from 17° to 18° centigrade, which is taken as the practical thermal unit and called the calorie, is always developed when $4{\cdot}184 \times 10^7$ ergs of work are expended in heat.

The second law.

If we try to bring about the reverse change and convert heat energy into mechanical work, experience shows that no heat engine will act if the whole of the available system is at a uniform temperature. Thus all steam engines have a boiler and a condenser, the atmosphere acting as condenser in the case of high-pressure engines. Oil engines work by the explosion of oil spray in the cylinder; a high temperature is thus produced, the atmosphere again acting as condenser. It will always be found that there is some heat given up to the condenser besides that which is transformed into work, and, in all cases, the heat is absorbed by the engine from the hotter parts of the system. Such observed facts can be generalized in the statement that it is impossible by inanimate mechanical means to obtain a continual supply of useful work by cooling a body below the temperature of the coldest of the surrounding bodies. It is possible to get a certain amount of work in this way, for instance, by allowing gas or vapour to expand, thus cooling itself and doing work; but a continual supply cannot be so produced. When the gas or vapour is used in a heat engine, and put through complete cycles of changes, an external supply of heat at a high temperature must be constantly maintained, and the engine will continually give up some of this heat to the cooler parts of the system.

It will now be seen that if a range of temperature is available, and a heat-engine be constructed to use it, the process will tend to diminish the difference of temperature between the parts of the system, heat passing from the hotter to the colder parts. Again, when heat flows by conduction, the transference always occurs in this same direction, and never in the reverse one. It is thus a general result of observation that heat cannot of itself, or by means of a self-acting mechanism, pass from a body of lower to a body of higher temperature.

This statement will be found to be equivalent to that enunciated above in the form that a continual supply of mechanical work cannot be obtained from the heat energy of the coldest part of the system. Both statements embody the

experimental generalization known as the second law of thermodynamics.

On the results of experience, as formulated in these two laws, the whole subject of thermodynamics is founded.

Work and energy.

When a force X moves its point of application through a distance dx, the work done by the force is $X.dx$, and, if the force acts on a system, this amount of energy is added to the system. Take as an example the case of a quantity of fluid confined in the cylinder of an engine (Fig. 1). If the piston be forced inwards, work is done on the system, and if the piston be allowed to move outwards, work is done by the system on the environment. If the area of the piston be A, and the pressure be p, the force is Ap, and if the piston rise through a small height dh, the work done by the contents of the cylinder is $Ap.dh$. But the change of volume of the working substance is $A.dh$, so that, representing the change of volume by dv, the work done is $p.dv$. In order to find the work done when a large volume change occurs, we must find the sum of all the separate values of $p.dv$. This process is termed integration, and is represented by the symbol $\int p\,dv$. When certain simple relations hold between the pressures and the volumes, we can find the value of this integral. For instance, if p remains constant throughout the operation, the sum of all the $p.dv$'s is the same as p multiplied by the sum of all the dv's, or $p(v_2 - v_1)$ where v_1 and v_2 represent the initial and final volumes. This constancy of pressure is practically attained when the working substance is a liquid in contact with its own saturated vapour: for instance, the water and steam in the boiler of an engine. If heat be supplied, evaporation goes on at constant temperature, and the pressure remains unchanged. Another important case arises when a gas, such as air, fills the cylinder. While the temperature keeps constant, the pressure is inversely proportional to the volume, and, as is well known, the whole

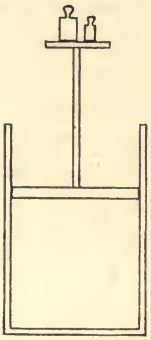


Fig. 1.

pressure, volume and temperature relations have been found experimentally to be represented very accurately by the equation

$$pv = RT,$$

where T is the temperature measured on the gas thermometer, of which the zero corresponds to $-273°$ centigrade, and R is a constant, the numerical value of which can be calculated for any given mass of gas. If we take as our unit mass the number of grams equal to the chemical constant known as the molecular weight of the gas (a number which is commonly called the gram-molecule), the volumes of different gases under the same conditions of temperature and pressure will be equal, and the value of R the same for all. The volume of the gram-molecule is found experimentally to be 22320 cubic centimetres when the pressure is that of the standard atmosphere (760 millimetres of mercury or 1·013 dynes per square centimetre) and the temperature is 0° centigrade, or 273° on the absolute scale of the gas thermometer. These numbers give for the value of R corresponding to the chemical unit of mass or the gram-molecule, $8{\cdot}284 \times 10^7$ ergs or 1·980 calories per degree centigrade. In approximate calculations R may therefore be taken as 2 calories per degree for each gram-molecule of gas.

As we have seen, the work done, while the volume changes from v_1 to v_2, is

$$\int_{v_1}^{v_2} p\,dv = \int_{v_1}^{v_2} \frac{RT}{v}\,dv.$$

For isothermal changes, both R and T are constant, and can be put outside the sign of integration. Now

$$RT \int_{v_1}^{v_2} \frac{1}{v}\,dv = RT \log_e \left(\frac{v_2}{v_1}\right) \ldots\ldots\ldots\ldots\ldots\ldots (1),$$

and thus we know the value of the work done by the gas when its volume increases at constant temperature. Similarly, when the volume is diminished, the same integral gives the work done on the gas.

These results can be well shown on a diagram (Fig. 2), in which the abscissae represent volumes and the ordinates pressures. On such a diagram the isothermal lines, defined by the relation that T and therefore pv is constant, will be rectangular

hyperbolas. Consider the work done while the gas passes from a state represented by the point A to a state represented by B.

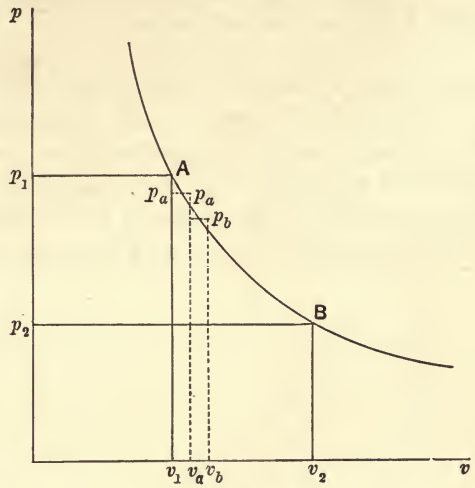


Fig. 2.

For a small change in volume v_1 to v_a, the pressure can be taken as constant, and the work, which is pdv, is represented by the area of the narrow strip $p_a p_a v_a v_1$. The work from v_a to v_b is measured by the area of the corresponding strip $p_b v_a v_b$, and it is now obvious that the total work from v_1 to v_2 is represented by the area of the figure ABv_2v_1 under the curve AB, which therefore is equivalent to the value of the integral $\int_{v_1}^{v_2} pdv$. Passing from A to B, the volume increases, and therefore work is done by the gas. If the process had been performed in the reverse order, from B to A, the work represented by the area would have been done on the gas, and the work done by the gas could be written $-\int_{v_2}^{v_1} pdv$.

Now $$pv = \text{constant};$$

hence differentiating, $$pdv + vdp = 0,$$

or $$-pdv = vdp.$$

Thus as regards the integrals

$$-\int pdv = \int vdp.$$

The latter integral is represented by the area ABp_2p_1 on the diagram, which is therefore equal to the area ABv_2v_1 as long as the curve is a rectangular hyperbola, that is, as long as Boyle's law holds good for the working substance.

Complete cycles.

Now let us imagine that the working substance, whatever it may be, is carried round a complete cycle of changes, so that in the end it is brought back to its original state, represented by A on the diagram. If the changes are not isothermal, the curve on the diagram can be made of any form we please. Thus on Fig. 3, let the cycle be

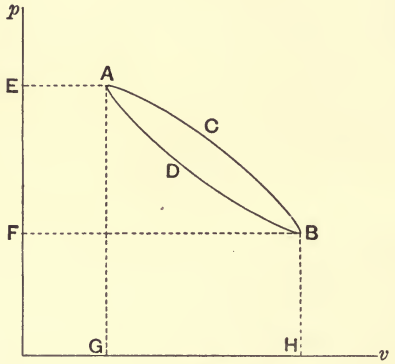


Fig. 3.

performed in the order $ACBDA$. The work done by the system along ACB is, as we have seen, measured by the area $ACBHG$, and that done on the system along BDA by the area $BDAGH$. The balance of work done by the system throughout the cycle is therefore the area $ACBHG$, less the area $BDAGH$, that is the area $ACBDA$ enclosed by the curve representing the successive states of the substance as regards pressure and volume. This area is measured by the integral $\int pdv$ taken all round the cycle. The area $ACBDA$ is also the difference between the areas $ACBFE$ and $BDAEF$, it can therefore be also represented by $-\int vdp$, which thus measures the work done in a complete cycle of any kind; while, when the cycle is not complete, this converse integral only measures

the work in the case of the isothermal changes in an ideal gas, the properties of which are exactly described by Boyle's law, pv is constant.

The relation

$$pv = \text{constant},$$

as we have seen, describes the behaviour of an ideal gas under isothermal conditions. The corresponding relation for adiabatic changes may be deduced by the help of the general equation which holds under all conditions for gaseous substances,

Adiabatic relations of an ideal gas.

$$pv = RT.$$

We must also remember that experiment has proved that there is only a very small change in the internal energy of a gas when its volume is changed isothermally, or, in other words, that no appreciable work is absorbed or liberated in merely separating the parts of the gas from each other. This work becomes less as the gas approaches the ideal condition, and may, for an ideal gas, be considered to be zero.

When a gas is heated at constant volume, no external work is done, and the whole of the heat energy is used in raising the temperature of the gas. On the other hand, if the pressure be constant, an amount of external work equal to $p\,dv$ is done. Let us express everything in mechanical units, and denote the specific heats at constant pressure and constant volume by C_p and C_v respectively. Then, considering unit mass and unit rise of temperature, we have, since the internal work is negligible,

$$C_p - C_v = p\,dv.$$

But the gas constant R is equal to pv/T, that is, to $p\,dv/dT$, or the pressure multiplied by the change in volume per degree. Hence

$$R = C_p - C_v.$$

Now for the general case, when a quantity of heat is allowed to enter an ideal gas, it is used in raising the temperature through a range which we will call dT, and in performing an amount of external work, which, for an infinitesimal change,

may be denoted by pdv. Thus, for an adiabatic process, when there is no gain or loss of heat,

$$C_v dT + p dv = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2).$$

Again from the equation

$$pv = RT,$$

we have, by differentiating,

$$p dv + v dp = R dT.$$

Substituting for dT in (2), and replacing R by $C_p - C_v$, we get

$$C_p p dv + C_v v dp = 0.$$

Then, denoting the ratio C_p/C_v by γ,

$$\gamma \frac{dv}{v} + \frac{dp}{p} = 0.$$

This ratio of the specific heats γ is found by experiment to be nearly independent of the pressure, volume and temperature. The equation can therefore be integrated. Thus

$$\gamma \log v + \log p = \text{constant},$$

or

$$pv^\gamma = \text{constant} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3),$$

the adiabatic relation required.

Reversible processes.

Let us imagine a quantity of water in contact with its vapour in an engine cylinder. It is known that, for a given temperature, there is one and only one pressure at which the system will be in equilibrium. If the pressure be slightly increased, vapour will condense till it again falls to its original value, or, if the excess of pressure be kept up, the whole of the vapour becomes liquid. Conversely, if the pressure be kept slightly below the equilibrium value, the whole of the liquid will evaporate. Either of these changes can be produced, theoretically at any rate, by a change of pressure infinitesimally small, if time enough is allowed. Similar changes can be produced if, instead of varying the pressure, the temperature be slightly altered, the least variation from the equilibrium value being enough to cause the system to move in one direction or the other. In such a case it is obvious that, when we have taken the system along a path ACB (Fig. 3) by

such infinitesimal changes, we can by similar infinitesimal changes in the other direction of the external variables, pressure or temperature, cause the same path to be described in the reverse direction. Such processes are called reversible, and it is clear that in practice, though we can never use infinitely slow variations and thus get strictly reversible processes, we can make the processes which actually go on more or less nearly reversible by keeping the changes in the external variables more or less slow.

It is evident that, to get reversible processes, we must keep the pressure and temperature indefinitely near their equilibrium values at all parts of the operations. If the temperature be kept constant, heat can be passed into the system while this condition is realized, provided that the temperature of the external source of heat, which must be higher than that of the working substance in order to produce a flow of heat at all, is made to differ from it by an amount infinitesimal only. The process is then very nearly reversible. Another case in which reversibility may be nearly attained arises when there is no passage of heat at all. The changes which then go on are called adiabatic. If the external pressure be kept indefinitely near that of the working substance throughout, such changes will be very nearly reversible.

A good example of changes practically adiabatic is found in the alterations of pressure and volume which accompany the passage of a wave of sound through air, the vibrations being so quick that there is no time for heat to enter or leave the parts of the air affected. This case may also be used to illustrate what occurs when the changes are neither isothermal nor adiabatic. If, for instance, the air remained compressed long enough for a flow of heat to occur from parts of the air which have been heated by the compression to parts which have been cooled by expansion, the conduction of heat could not be reversed by an infinitesimal change of temperature, and the process becomes irreversible.

It will be noticed that, for a process to be reversible in the thermodynamic sense of the word, it is not enough that it can be made to proceed in the reverse direction. It is also necessary

that this change in the direction of the process should be effected by a change of an infinitesimal amount in the external conditions. No real process can be an exactly reversible one, though physical and chemical actions which are not accompanied by anything of the nature of friction, can be made almost reversible by keeping the conditions very near those of equilibrium, and the action consequently slow. Viscous forces, such as those which a liquid offers to the passage of a body through it, do not interfere with this result, for they may be made indefinitely small by reducing indefinitely the velocity of change. The existence of viscosity, then, does not prevent a system undergoing reversible operations. Ordinary friction, on the other hand, such as that between solid surfaces, restrains a system from change till the driving forces reach a finite value, and entirely prevents even an approximation to a condition of reversibility.

Thus, although reversibility can never be attained in practice, systems can be divided into those which can be made very nearly reversible, and those which cannot. The directive forces of the former could be diminished without limit as the changes in them become indefinitely slow; they are therefore called reversible systems.

A similar distinction can be drawn between the equilibria of these two classes of systems. The weight of a body hanging by a spring is balanced by the force exerted by the spring, and the body will move in one direction or the other as the weight is increased or diminished by a very small amount. So a liquid in contact with its own vapour is in equilibrium when the rates of evaporation and condensation are equal. A solid is in equilibrium with its solution when the amount dissolved per second is equal to the amount precipitated. Such cases of true equilibrium are at once known by the fact that a small change in one of the external conditions, temperature or pressure, will at once cause a corresponding change in the factors of equilibrium; more liquid will evaporate or condense, or more solid go into or out of solution.

But equilibrium often exists which is not the effect of the balance of such oppositely directed active tendencies. A body

can be kept on an inclined plane by the roughness of the surfaces in contact; and so some physical and chemical transformations may possibly be prevented by forces analogous to friction. Such forces might be overcome by changing the conditions: for example, by heating some explosive substances which are unchangeable at ordinary temperatures; but, as long as the frictional forces keep the system in equilibrium, it will not be disturbed by any small change in the external conditions. Thus it is thought a false equilibrium may be distinguished from a true one. On the other hand, viscous resistances, like those exerted on a moving body by fluids, delay but do not prevent motion, and will not affect the final conditions of true equilibrium. The equilibrium reached, then, will, if we wait long enough, be independent of all such viscous forces.

Now the importance of this distinction between true and false equilibrium lies in the fact that, while the first law of thermodynamics, the principle of the conservation of energy, holds good for all processes whatever, the second law can only be applied to obtain quantitative results in a system which exists in true equilibrium. Such a system will respond to a slight change in external conditions. It is therefore strictly reversible and capable of being taken reversibly through a complete cycle of operations, and can finally be brought back to exactly that state from which it started, each part of the change being reversible. As we have seen, a very slow physical or chemical change is reversible when an indefinitely small alteration in one of the external conditions, such as temperature or pressure, is enough to reverse the direction in which the change proceeds. Thus the system must at each instant be indefinitely near its equilibrium condition. A good example of such an arrangement, described above, is seen when a liquid is in contact with its own saturated vapour at a given temperature. By bringing it into contact with a body at a temperature higher than its own by an infinitesimal amount, heat slowly enters the system, liquid evaporates and external work can be done. On replacing the source of heat by a body the temperature of which is infinitesimally lower, the direction of flow of heat will change, and energy will

be absorbed by the system, showing that the process is reversible.

Similar considerations apply to all processes where a true chemical or physical equilibrium exists. The systems are reversible, and can be carried through complete cycles of changes. Examples, such as the evolution of carbon dioxide from calcium carbonate or the solution of a solid in water, are numerous. But the second law of thermodynamics has sometimes been applied to cases of false equilibrium, equilibrium maintained by frictional forces, and to chemical actions, explosions and the like, which are not reversible, and cannot be carried through a cyclical process. Such applications are not legitimate, and the conclusions reached, though they may be correct expressions of tendencies, are not exact results.

Reversible engines.

To study the laws which describe the transference of heat into work, it is best to examine the simplest possible form of engine, consisting of a cylinder wherein is confined some substance, the volume of which depends on the temperature. The walls of the cylinder are perfect non-conductors of heat, and its bottom a perfect conductor. By putting the cylinder on a non-conducting stand, the contents are thermally isolated, and by transferring it to a conducting body of large size they are placed in isothermal conditions and an indefinite supply of heat can be admitted or abstracted. Two such bodies are needed, one at a high temperature, one at a low temperature. We now have an engine reduced to its simplest form. In order to draw valid conclusions about the heat absorbed and the mechanical energy developed, we must put the engine through a complete cycle, and bring the working substance back to its original state: its internal energy will then be the same as it was at first, and any work done must be due to the heat energy absorbed from the surroundings. This simplest theoretical form of engine was first described by Carnot, who revolutionized this branch of physics by calling attention to the importance of considering complete cycles of operations.

We have already deduced the conditions of reversibility,

and have seen that the co-ordinates which determine the state of the substance must, at any instant, differ only infinitesimally from their equilibrium values. Now the simplest reversible cycle we can arrange consists of four processes, illustrated graphically by the diagram of Fig. 4.

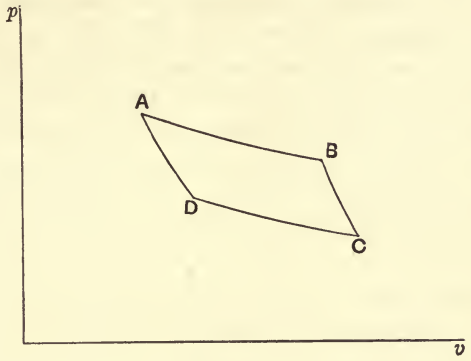


Fig. 4.

(1) Allow the substance to expand isothermally in contact with the hot body from the state *A* to the state *B*.

(2) Thermally isolate the substance, and continue the expansion adiabatically from *B* to *C*.

(3) Transfer the cylinder to the cold enclosure, and compress it isothermally from *C* to *D*.

(4) Again isolate the cylinder, and compress it adiabatically till the working substance again reaches the state defined by *A*.

It will be observed that, since the temperature is, on the average, higher during the processes (1) and (2) than it is during (3) and (4), the pressure must be higher also, and therefore more work is done by the substance in expanding than is done on it while contracting. On the whole, then, a balance of useful work is performed by the engine, and this work has been obtained at the expense of some of the heat absorbed from the surroundings during process (1); for the quantity of heat given up to the environment during process (3)

is less than that absorbed during (1) by an amount dynamically equivalent to the balance of work done.

Now, in order that this cycle should be performed at all, the external conditions of temperature and pressure must differ appreciably from their equilibrium values, but to insure the reversibility of the cycle, they must only differ by infinitesimal amounts. Nevertheless, although the required conditions cannot be obtained, theoretically the cycle is a reversible one, and we can imagine each process performed in the reverse order, heat being taken in at the low temperature, a balance of work being done on the substance, and the thermal equivalent of this work added to the heat absorbed, and given out with it as a larger quantity of heat at the higher temperature. The whole cycle, and all the individual parts of it are theoretically reversible.

In no actual engine can a reversible cycle be obtained, and, if an indicator diagram, as it is called, be drawn to represent the relation at each instant between the pressure and the volume of the steam in the cylinder, and its form compared with the isothermal and adiabatic lines for saturated steam, it will be seen in what ways the engine fails. Since the working substance must be colder than the source of heat and warmer than the condenser, and partly also in consequence of the unavoidable thermal losses which will occur, the top and the bottom of the indicator diagram will be nearer together than in the theoretical diagram of Fig. 4, the corners will be rounded off and the available area, that is the work done, will be less.

In fact, it can be shown that a reversible engine is the theoretically perfect engine, and has the highest efficiency which an engine can possess: it will transform the greatest possible fraction of the heat absorbed into useful mechanical work. For, if possible, let an engine have a greater efficiency than a reversible engine, and let us use it in conjunction with a reversible engine in such a way that it works the reversible engine backwards over the cycle of Fig. 4, putting work into it, and forcing it to give up heat to the hot reservoir, which is common to the two engines. The more efficient engine is at

the same time constantly taking a supply of heat from this reservoir, and, in virtue of its assumed efficiency, it can perform the work required, that is to keep the reversible engine in operation, by using a smaller quantity of heat than the reversible engine returns to the hot reservoir. This excess must be obtained from the cold reservoir, and therefore the combined machine enables heat to pass regularly and automatically from a cold to a hot body. Such a result is contrary to experience; it proves that our hypothesis is false, and that no imaginable engine can possess a greater efficiency than a reversible engine. We have already seen that no actual engine can do the amount of work corresponding to a strictly reversible cycle. It therefore follows that no other engine can have as great an efficiency as a reversible engine.

The absolute scale of temperature.

A reversible engine, then, has the maximum efficiency possible and we need not limit ourselves in choosing the working substance. Any system, the volume of which depends on temperature, might be used. The efficiency of a reversible engine is thus independent of the nature of the working substance and of the kind of process employed. It depends only on the temperatures of the hot and cold bodies which are used as the source of heat and as the condenser of the engine. Now the efficiency of an engine, the fraction of the heat taken in which is transformed into work, can be expressed in terms of the heat changes only, for by the principle of the Conservation of Energy, if H_1 is the quantity of heat absorbed from the hot reservoir, and H_2 the quantity of heat given out to the cold reservoir, the work done must be equivalent to their difference, and the efficiency must be

$$\frac{H_1 - H_2}{H_1}.$$

Thus H_2/H_1, which is obtained by subtracting this expression from unity, must also depend only on the temperatures. But any property which depends only on the temperature can be used as a means of measuring temperature, just as the change in volume of mercury is used as a means of measuring

temperature in the common mercury thermometer. We may thus agree to compare two temperatures by finding the ratio of the quantities of heat absorbed and ejected by a perfect reversible engine working between those temperatures. Then denoting by θ_1 and θ_2 the temperatures as thus defined,

$$\frac{\theta_1}{\theta_2} = \frac{H_1}{H_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4),$$

and this thermodynamic temperature scale, unlike those which depend on any one property of a particular substance, such as the volume relations of mercury or the like, is a true absolute scale.

Moreover this scale of temperature is a consistent one: for if a second reversible engine be coupled with the first, taking in as its supply of heat at θ_2 the heat given out to its condenser by the first engine, the ratio of the heat taken in at θ_1 to that finally given out at θ_3 by the compound engine will be

$$\frac{H_1}{H_2} \cdot \frac{H_2}{H_3} = \frac{\theta_1}{\theta_2} \cdot \frac{\theta_2}{\theta_3},$$

giving the same formula as before,

$$\frac{H_1}{H_3} = \frac{\theta_1}{\theta_3}.$$

It remains to connect this absolute scale of temperature with some scale which can be practically constructed. Now, since all reversible engines have the same efficiency, to calculate the efficiency of any one such engine is to know that of all. It is easy to find the ratio of the heats taken in and given out by an engine using as its working substance a gas which is described by the laws of Boyle and Charles and suffers no changes of internal energy when its volume varies isothermally. Experiments can afterwards be made to determine how far any known gas departs from those ideal relations. We have seen that a simple reversible cycle may be performed by means of isothermal and adiabatic processes; the experimental gaseous laws show that isothermal changes can be represented by the expression

$$pv = \text{constant},$$

while we have already deduced the adiabatic relation,

$$pv^\gamma = \text{constant.}$$

Let us then take unit mass of an ideal gas through a simple cycle like that described above. As we see by equation (1) on p. 4, during an isothermal expansion at a temperature T_1, an amount of work is done by the gas equal to $RT_1 \log \frac{v_2}{v_1}$.

Similarly the work done on the gas during the isothermal contraction at T_2 is

$$-RT_2 \log \frac{v_4}{v_3} = RT_2 \log \frac{v_3}{v_4}.$$

If the gas absorbs no internal work, that is, if no energy is needed to separate or concentrate the molecules, these expressions for the external work done by the gas can also be taken as giving the heat absorbed and ejected during each process. Thus

$$\frac{H_1}{H_2} = \frac{RT_1 \log v_2/v_1}{RT_2 \log v_3/v_4}.$$

Now the change from v_1 to v_2 is isothermal and

$$p_1 v_1 = p_2 v_2.$$

Similarly $$p_4 v_4 = p_3 v_3.$$

Dividing the first of these equations by the second

$$\frac{p_1 v_1}{p_4 v_4} = \frac{p_2 v_2}{p_3 v_3} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5).$$

Again the changes from v_2 to v_3 and from v_4 to v_1 are adiabatic, and therefore

$$p_1 v_1^\gamma = p_4 v_4^\gamma \text{ and } p_2 v_2^\gamma = p_3 v_3^\gamma.$$

Hence $$\frac{p_1 v_1^\gamma}{p_4 v_4^\gamma} = 1 = \frac{p_2 v_2^\gamma}{p_3 v_3^\gamma} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6).$$

Dividing (6) by (5) and clearing the indices

$$\frac{v_1}{v_4} = \frac{v_2}{v_3} \text{ or } \frac{v_2}{v_1} = \frac{v_3}{v_4}.$$

We therefore have

$$\frac{H_1}{H_2} = \frac{RT_1 \log v_2/v_1}{RT_2 \log v_3/v_4} = \frac{T_1}{T_2} \quad \ldots\ldots\ldots\ldots\ldots (7),$$

and thus find that the thermodynamic temperatures are the same as those measured on an ideal gas thermometer. Experiments have shown that an air or hydrogen thermometer agrees very nearly indeed with the ideal gas thermometer.

We may therefore take the air thermometer as giving a very near approximation to the absolute thermodynamic scale, and write indiscriminately θ_1, θ_2 or T_1, T_2.

Complex cycles.

The cycle of Fig. 4, consisting of two isothermal and two adiabatic processes, is the simplest form of reversible cycle, but any curve on the pressure-volume diagram can represent a reversible cycle if the external conditions are kept throughout indefinitely near their equilibrium values. A closed curve, such as that in Fig. 5, can be described by taking the substance through small isothermal and adiabatic changes alternately, as indicated in the figure. If these changes are small enough, the lines representing them practically become the closed curve, and the cycle remains reversible.

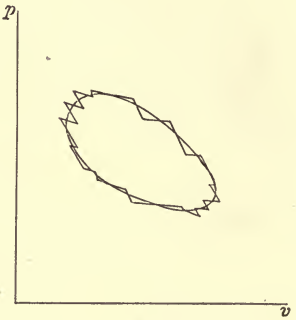


Fig. 5.

Generalized co-ordinates.

We have hitherto expressed the work done on or by the system as the product of a force and a length or of a pressure and a volume; but the same energy dimensions can be obtained as the product of many other pairs of quantities, such as surface tension and area, electromotive force and quantity of electricity, etc. Each of these products consists of a coordinate defining some quantity in the system (volume, quantity of electricity, etc.) and a term often called an intensity factor (pressure, electromotive force, etc.), analogous to the force in the first case.

Now, in the general case, the work done by a system may contain all such possible products, and its expression will then involve a series of terms

$$X_1\delta x_1 + X_2\delta x_2 + X_3\delta x_3 + \ldots\ldots$$

The factors X_1, X_2, etc. are the intensity factors or the "generalized forces," though, as we have seen, they are not all necessarily of the physical dimensions of real forces, and x_1, x_2, etc. may similarly be called the quantity factors or the "generalized coordinates."

All the forms of energy thus considered are mutually convertible and, if perfect machines could be obtained, completely convertible. Thus, the whole of a quantity of mechanical energy might, by the aid of a theoretically perfect dynamo, be transformed into electrical energy, while the electrical energy might drive a motor and be reconverted, theoretically without loss. All such forms of energy are therefore said to have the same value, and may be grouped in a single term, which may for convenience be written as

$$\Sigma\,(X\delta x).$$

Internal energy.

The fact that heat cannot in general be completely converted into other forms of energy, shows that it is not of the same value as they are, and should be represented by a separate term in the expression for the energy. The equation giving the increase in total energy ϵ of a system which takes in a quantity of heat δH, and also absorbs various kinds of external work, represented by $\Sigma\,(X\delta x)$, may therefore, in accordance with the first principle be written

$$\delta\epsilon = \delta H + \Sigma\,(X\delta x).$$

Now the internal energy of a body is, by the principle of conservation, the same when the body is in a given state, whatever its previous history has been; thus a change in energy can be expressed as the difference between the absolute values of the energy content of the system, and for finite changes we may write

$$\epsilon_B - \epsilon_A = \int_A^B \left\{\delta H + \Sigma\,(X\delta x)\right\},$$

where the integral refers to any path of change between the states A and B.

Entropy.

For a simple reversible cycle, between two temperatures θ_1 and θ_2, we have seen that

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2}.$$

Treating heat taken into the system as positive and that given out as negative, this is equivalent to the statement that

$$\frac{H_1}{\theta_1} + \frac{H_2}{\theta_2} = 0.$$

Similarly for any complex reversible cycle such as that illustrated by Fig. 5, the same principle holds and

$$\int \frac{dH}{\theta} = 0.$$

If the operations are not reversible, the efficiency of the cycle must, as we have seen, be less, thus

$$\frac{H_1 - H_2}{H_1} < \frac{\theta_1 - \theta_2}{\theta_1};$$

or, subtracting unity from each side, we deduce

$$\frac{H_1}{\theta_1} + \frac{H_2}{\theta_2} < 0,$$

and for a complex non-reversible cycle the corresponding relation is

$$\int \frac{dH}{\theta} < 0.$$

Now, if the system can pass from a state A to a state B in two different ways, each reversible, we can take the system from A to B along one of them and back from B to A along the other. Then for the complete cycle

$$\int_A^B \left(\frac{dH}{\theta}\right)_I + \int_B^A \left(\frac{dH}{\theta}\right)_{II} = 0,$$

where the suffixes I and II refer to the two different paths.

Thus
$$\int_A^B \left(\frac{dH}{\theta}\right)_I - \int_A^B \left(\frac{dH}{\theta}\right)_{II} = 0,$$

or
$$\int_A^B \left(\frac{dH}{\theta}\right)_I = \int_A^B \left(\frac{dH}{\theta}\right)_{II},$$

the value of the integral being the same for all reversible paths.

This integral may therefore be taken as representing the difference in value of some definite quantity characteristic of the system in each of the states A and B, and we may write

$$\int_A^B \frac{dH}{\theta} = \phi_B - \phi_A.$$

This function ϕ is called the "entropy" of the system.

For a small reversible change in any system, we have thus, as the expression of the second principle of thermodynamics,

$$\frac{\delta H}{\theta} = \delta\phi \text{ or } \delta H = \theta\delta\phi,$$

while, if the change is a non-reversible one,

$$\delta H < \theta\delta\phi,$$

ϕ in each case being a function of the constitution of the system in its given state and independent of its previous history.

These relations are well illustrated by the diagrams already used. For an infinitesimal reversible transfer of heat, the change from the isentropic line along which the entropy is constant and represented by ϕ to that along which it is represented by $\phi + \delta\phi$ takes place by the isothermal along which the temperature is θ; the heat absorbed, δH, being equal to the area $\theta\delta\phi$.

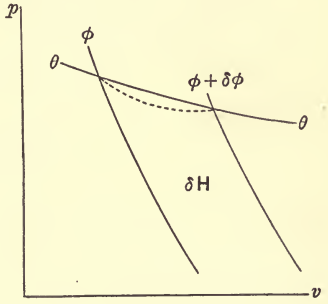


Fig. 6.

For any actual change, however, the path will not be isothermal, and we get a non-reversible path, such as the dotted line of Fig. 6, in which case the area δH is less than $\theta\delta\phi$.

For reversible changes, we see from the expression for the change in heat energy,

$$\delta H = \theta\delta\phi,$$

that the entropy ϕ may be considered as the quantity factor in the heat energy of a system, just as x is the quantity factor in

the generalized expression for the work $X\delta x$; it corresponds to the quantity of electricity, for example, in the expression for the electrical work $E\delta q$, or to the area in the expression for the surface energy $S\delta A$, where S is the surface tension. From this point of view, the temperature, θ, represents the intensity factor in the heat energy.

If the system is isolated, δH is zero, and the condition of reversibility is

$$\theta\delta\phi = 0,$$

while for non-reversible changes

$$\theta\delta\phi > 0.$$

Thus the minimum possible value of $\theta\delta\phi$ is 0, while for all actual changes it has a greater value, and it follows that every possible change in the system is attended by an increase in the entropy. Therefore in an isolated system, stable equilibrium is attained when the entropy is at a maximum, for no further spontaneous change can occur.

In order to obtain a clearer idea about the nature of entropy, we may write the equation

$$\delta\phi = \frac{\delta H}{\theta}$$

in the form

$$\frac{d\phi}{d\theta} = \frac{1}{\theta}\frac{dH}{d\theta}$$

which shows that the change of entropy per degree is equal to the specific heat of the substance under the given conditions, divided by the absolute temperature. In considering finite changes, it is necessary to notice that we no more want to know the absolute value of the entropy of a body than the absolute value of the energy. In each case it is with the changes in the value that we are alone concerned. The equation can be integrated in certain cases where the relations between the properties of the substance are simple, as, for instance, in an ideal gas. Here the internal work is zero, and any heat applied is used in raising the temperature and in doing external work. Now the specific heat, C_v, of a gas

at constant volume is the heat required to raise unit mass one degree without doing external work, thus

$$\delta H = C_v \delta\theta + p\,\delta v,$$

$$\delta\phi = \frac{\delta H}{\theta} = \frac{C_v \delta\theta}{\theta} + \frac{p\,\delta v}{\theta}$$

$$= C_v \frac{d\theta}{\theta} + R\frac{dv}{v};$$

so that, integrating,

$$\phi_2 - \phi_1 = C_v \log\frac{\theta_2}{\theta_1} + R\log\frac{v_2}{v_1}.$$

From this equation it is easy to calculate the change in entropy corresponding to any given alteration in the state of the gas.

Thermodynamic potential.

When the system is not isolated, further considerations are involved. The first law gives as the change in energy in a system

$$\delta\epsilon = \delta H + \Sigma\,(X\,\delta x),$$

which, by the second law, gives for a reversible transformation

$$\delta\epsilon = \theta\,\delta\phi + \Sigma\,(X\,\delta x).$$

Subtract from each side

$$\delta\,(\theta\phi) = \theta\,\delta\phi + \phi\,\delta\theta,$$

then

$$\delta\,(\epsilon - \theta\phi) = -\phi\,\delta\theta + \Sigma\,(X\,\delta x).$$

Again, taking the equation

$$\delta\epsilon = \theta\,\delta\phi + \Sigma\,(X\,\delta x),$$

subtract

$$\delta\,\{\theta\phi + \Sigma\,(Xx)\} = \phi\,\delta\theta + \theta\,\delta\phi + \Sigma\,(X\,\delta x) + \Sigma\,(x\,\delta X),$$

then

$$\delta\,\{\epsilon - \theta\phi - \Sigma\,(Xx)\} = -\phi\,\delta\theta - \Sigma\,(x\,\delta X).$$

If we write ψ for $(\epsilon - \theta\phi)$ and ζ for $\{\epsilon - \theta\phi - \Sigma\,(Xx)\}$ the two equations become

$$\delta\psi = -\phi\,\delta\theta + \Sigma\,(X\,\delta x) \ldots\ldots\ldots\ldots\ldots\ldots (8),$$

$$\delta\zeta = -\phi\,\delta\theta - \Sigma\,(x\,\delta X) \ldots\ldots\ldots\ldots\ldots\ldots (9),$$

these expressions again characterizing reversible changes. For non-reversible transformations the relation yields

$$\delta\psi < -\phi\delta\theta + \Sigma(X\delta x),$$
$$\delta\zeta < -\phi\delta\theta - \Sigma(x\delta X).$$

Let us apply these results to two special cases:

(1) When the temperature and the generalized external coordinates $x_1, x_2 \ldots$ are constant, and consequently $\delta\theta$ and δx vanish and

$$\delta\psi < 0,$$

that is, $\delta\psi$ must be negative, and a transformation of the system is only possible if it decreases ψ.

(2) When the temperature and the generalized external forces $X_1, X_2 \ldots$ are constant, so that $\delta\theta$ and δX vanish, we have

$$\delta\zeta < 0,$$

and a change is only possible if it decreases ζ.

Thus in the first case, when θ and x are constant, equilibrium is only possible when ψ is a minimum; in the second case, when θ and X are constant, when ζ is a minimum.

Now in dynamics a mechanical system is in equilibrium when its mechanical potential is a minimum; thus ψ and ζ are functions analogous to potential in dynamics, and are hence known as thermodynamic potentials.

When the generalized co-ordinates $x_1, x_2 \ldots$ are constant, no external work is done, and the changes which occur involve internal variables alone; for this reason ψ is sometimes known as the internal thermodynamic potential. Constancy of the external generalized forces, however, does not prevent external work, which is equal to $\Sigma X\delta x$; thus ζ has been called the total thermodynamic potential.

In many of the systems studied in thermodynamics, it is possible to exclude electrical and other similar actions. The only external co-ordinate is then the volume, and the only external generalized force which the system exerts is a uniform normal pressure p. The equations then simplify to

$$\delta\psi = \delta(\epsilon - \theta\phi) = -\phi\delta\theta - p\delta v,$$
$$\delta\zeta = \delta(\epsilon - \theta\phi - pv) = -\phi\delta\theta + v\delta p.$$

In isothermal systems, equilibrium is reached at constant volume when ψ is a minimum, and at constant pressure when ζ is a minimum. On this account ψ has sometimes been called the thermodynamic potential at constant volume and ζ the thermodynamic potential at constant pressure.

Conditions of equilibrium.

We have thus deduced conditions of equilibrium in the three cases which are of practical importance:

(1) In an isolated system, the entropy must be a maximum.

(2) In an isothermal system, when the external coordinates are constant, ψ must be a minimum.

(3) In an isothermal system, when the external generalized forces are constant, ζ must be a minimum.

Application of thermodynamic potential.

The numerical values of the thermodynamic potentials can only be calculated for certain cases, but the mere existence of such functions, as determining the conditions of equilibrium of isothermal systems, enables many useful deductions to be made.

Let us, for example, consider the conditions of equilibrium between a solid and a solution of it in some liquid, the whole system being maintained at constant temperature and constant pressure. Since the ζ function must be a minimum, the dissolution or precipitation of a small quantity of solid will not change its value. Now if the solid phase increase by a small mass δm, and the liquid phase decrease by an equal amount, the rates of increase and decrease of the ζ functions for the two phases will be given by the partial differential coefficients $\partial\zeta_1/\partial m$ and $\partial\zeta_2/\partial m$ and the condition of equilibrium is that

$$\frac{\partial\zeta_1}{\partial m} = \frac{\partial\zeta_2}{\partial m}.$$

The common values of these differential coefficients give the amount of work necessary to introduce unit mass of each substance into any of the phases or states under the conditions of the system, and are termed by Gibbs[1] "the chemical

[1] *Trans. Conn. Acad.* vol. III. 1877, translated *Thermodynamische Studien*, Leipzig, 1892, and *Equilibre des Systèmes Chimiques*, Paris, 1899.

potentials" or "the potentials" of the substances in the given phases or states.

A graphical method, due to van Rijn van Alkemade[1] enables us to treat the subject in a simple manner.

Let the abscissae (Fig. 7) denote the number of gram-molecules of solvent in which one gram-molecule of the solid is dissolved, and the ordinates be proportional to the value of the ζ function for unit mass of the phase considered.

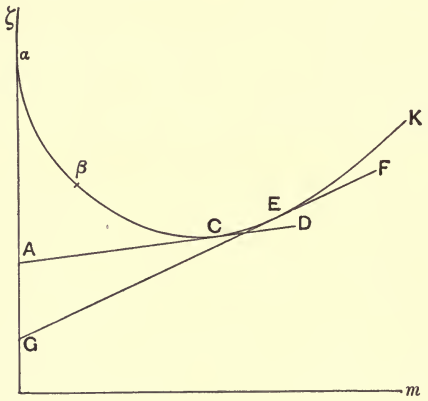


Fig. 7.

First consider the curve for the liquid phase, which gives the value of ζ for unit mass of the phase as the amount of solvent containing one gram-molecule of solute changes from zero to infinity. When m vanishes, ζ has the value corresponding to the solute in its liquid form: a fused salt, for example. The direction of the curve is determined by the gradient $d\zeta/dm$. When m is small, and the concentration of the water in the fused salt is therefore small, the amount of work required to introduce a further small quantity of water will be given by an expression analogous to that which holds for a gas, which is essentially only a dilute system (see p. 4). The value of $d\zeta/dm$ will therefore be of the form $a + \log bm$ where a and b are independent of m. When m is zero this

[1] *Zeits. physikal. Chem.* II. 289, 1893.

expression becomes $-\infty$, and therefore the curve must at first touch the axis of ζ. As m increases, it must leave the axis of ζ, and, when m is infinite, ζ reaches its value for pure water. The value of $d\zeta/dm$ is then the work done in adding a gram-molecule of water to an infinitely dilute solution, and denotes the potential of pure water. For large values of m, then, $d\zeta/dm$ must approach a constant value, and finally the curve must become a straight line.

Let a curve which satisfies these conditions be drawn, and taken to represent the changes in ζ as the composition of the liquid phase changes. Such a curve is $\alpha\beta CK$.

The composition of the solid phase does not vary, and is fixed by the condition that m is zero.

At temperatures below the melting point of the solid, the fused substance will pass spontaneously into the solid form, and therefore the value of ζ for unit mass of the substance must be less in the solid than in the liquid form. Thus the point representing the value of ζ for the solid solute must lie below the point α, which represents the value for the fused solute. Let the value of ζ for the solid be represented by A.

Now let us trace what happens when a dilute solution is isothermally evaporated at constant pressure. The potential of the liquid phase is represented for each concentration by the tangent to the curve. As long as these tangents cut the ζ axis below the point A, as in the case of the line FEG, the potential of the system as liquid is less than that of the other possible arrangement consisting of a certain amount of saturated solution and a certain amount of the solid, and no precipitation occurs. But when the tangent reaches A, as does the line DCA which touches the curve at the point C, the value of $d\zeta/dm$ is the same for the liquid phase as for the mixture of saturated solution and solid, and equilibrium between solution and solid is therefore possible. Beyond the point C, the tangents cut the axis above A, and the potential of the liquid is greater than that of the system containing the solid. The solution is unstable, and the curve $C\beta\alpha$ represents supersaturated solutions, ending in the undercooled fused solute, the value of ζ for which is represented by α. The values of the ζ function for unit mass of the system made

up of the various mixtures of the solid with its saturated solution are represented by the points on the straight line CA. At A there is no solvent, and thus no solution; at C the amount of solvent is just enough to dissolve all the solid.

We shall find later that a consideration of the possible forms of these ζ curves, throws much light on the special phenomena of the equilibrium of different phases.

We have proved on p. 23 the relations

Free energy.

$$\delta\psi = -\phi\delta\theta + \Sigma(X\delta x)$$

and

$$\delta\psi < -\phi\delta\theta + \Sigma(X\delta x)$$

for reversible and non-reversible changes respectively. When the conditions are isothermal, $\phi\delta\theta$ vanishes and

$$\delta\psi \leqq \Sigma(X\delta x) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10).$$

But $\Sigma(X\delta x)$ denotes the external work taken in by, and therefore $-\Sigma(X\delta x)$ the external work which can be obtained from the system during an infinitesimal, isothermal variation. If we denote by W the work which the system can give in passing isothermally from a state A to a state B,

$$\psi_B - \psi_A \leqq \int_A^B \Sigma(X\delta x) = -W,$$

thus

$$W \leqq \psi_A - \psi_B,$$

or, the work obtainable from the system during a finite isothermal change of state is equal to the decrease in its internal thermodynamic potential for a reversible process, and is less than that decrease for a non-reversible process. The decrease in the function ψ therefore denotes the maximum amount of available energy which can be extracted as mechanical work from a system during isothermal processes, and ψ has on this account been called by Helmholtz the free energy of the system.

From the equation

$$\delta\psi = -\phi\delta\theta + \Sigma(X\delta x)$$

we have, when $x, \ldots$ is constant,

$$\phi = -\frac{d\psi}{d\theta};$$

but ψ was defined by the relation

$$\psi = \epsilon - \theta\phi,$$

thus, the equation of free energy may be put in the form

$$\psi = \epsilon + \theta \frac{d\psi}{d\theta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11),$$

expressing the relation between the free energy, the total energy and the temperature.

Application of the free energy principle.

If we know the expression for the work which the system can do in any case, the value of ψ can be determined. As an example, let us deduce the well-known latent heat equation. In the case of a change of volume, the external energy factors are pressure and volume, and, when the pressure is constant as in the isothermal evaporation of a liquid or fusion of a solid, the work done in that isothermal operation while the volume increases from v_1 to v_2 is $p(v_2 - v_1)$ so that

$$\frac{d\psi}{d\theta} = -\frac{dp}{d\theta}(v_2 - v_1).$$

But the principle of the conservation of energy shows that the increase of internal energy of a system is equal to the difference between the heat absorbed and the work done by it, or

$$\epsilon = H - W.$$

For a reversible change $W = -\psi$ and we have $H = \psi - \epsilon$.

Substituting in the equation of free energy

$$\psi = \epsilon + \theta \frac{d\psi}{d\theta},$$

we find

$$H = -\theta \frac{d\psi}{d\theta}.$$

The heat absorbed, H, may here be written as λ, the latent heat of fusion or evaporation respectively of one gram-molecule of the substance; thus

$$\lambda = \theta \frac{dp}{d\theta}(v_2 - v_1), \text{ or } \frac{dp}{d\theta} = \frac{\lambda}{\theta(v_2 - v_1)} \ldots\ldots\ldots (12).$$

Special problems of thermodynamics can often be treated by a direct application of the expression for the efficiency of a

reversible cycle, which states that the balance of useful work obtained from the system when the temperature range between its terminals is $\delta\theta$, is given by

$$\delta W = H \frac{\delta\theta}{\theta}.$$

Now if the working substance is a liquid in contact with its own saturated vapour, the pressure during an isothermal change is constant. If the difference between the temperatures is infinitesimal, the indicator diagram becomes a narrow horizontal strip, the area of which is independent of the nature of its ends. The rate of change of the saturation pressure with temperature being $dp/d\theta$, the breadth of the strip is $(dp/d\theta)\,\delta\theta$ and its area, measuring the effective work during a complete cycle is $\{(dp/d\theta)\,\delta\theta\}\,(v_2 - v_1)$. The efficiency equation then becomes

$$\frac{dp}{d\theta}\,\delta\theta\,(v_2 - v_1) = H \frac{\delta\theta}{\theta}.$$

We are therefore again led to the latent heat equation

$$\lambda = \theta \frac{dp}{d\theta}\,(v_2 - v_1).$$

The process of evaporation involves, in general, an increase in volume, so that $v_2 - v_1$ is a positive quantity. The sign of $dp/d\theta$, therefore, must be the same as that of λ, the latent heat. Thus if, as is usual, heat must be supplied to evaporate a liquid, the sign of $dp/d\theta$ is positive, and the vapour pressure increases with rise of temperature.

When a solid is fused, however, the volume change is sometimes negative, that is to say, there is a contraction when the solid becomes a liquid, as in the case of water. λ being still positive, this makes $dp/d\theta$ negative, and the pressure falls as the temperature rises. This pressure is, of course, the pressure under which ice is in equilibrium with water, and the negative sign of its differential coefficient shows that the freezing point of water is lowered by pressure.

It is easy to calculate the numerical value of this lowering for the additional pressure of one atmosphere, that is, when δp is $760 \times 13{\cdot}6 \times 981$ or $1{\cdot}014 \times 10^6$ dynes per square centi-

metre. The freezing point of water is 273° on the absolute scale, λ, the latent heat of fusion of one gram-molecule of ice, is $18 \times 79{\cdot}4$ thermal units or $1431 \times 4{\cdot}184 \times 10^7$ ergs, and $v_2 - v_1$ is $-0{\cdot}0908 \times 18$ cubic centimetres. Thus

$$\delta\theta = \frac{\theta(v_2 - v_1)}{\lambda}\delta p = -0°{\cdot}00756.$$

When the solid is denser than the liquid, as it is in most substances other than water, $dp/d\theta$ is positive, and the freezing point is raised by pressure.

Note. In deducing the latent heat equation by means of a reversible cycle, it is necessary to suppose that the range of temperature is infinitesimally small, for, if it be finite, it will not, in general, be possible to carry the sytem from a state of saturation at a temperature θ to a state of saturation at $\theta - \delta\theta$ by a wholly adiabatic process of cooling. Moreover, the quantity of work done during this operation will depend on the amount of the liquid left, which has also to be cooled by the expansion of the vapour. Thus, the system must

(1) expand isothermally at θ till all the liquid is evaporated;

(2) expand adiabatically in dust-free space, so that there is no condensation, till the temperature falls to $\theta - \delta\theta$ (the pressure not being determined);

(3) pass in one direction or the other along the lower isothermal till the saturation pressure $p - (dp/d\theta)\,\delta\theta$ is reached, and then condense to liquid along the same isothermal;

(4) be compressed adiabatically as liquid till the temperature rises to θ; and, finally, as part of (1) pass along the isothermal θ till the original condition is once more attained.

It is now obvious that only when the temperature range is infinitesimal can the work done in (2) and (4) be neglected compared with that done in (1) and (3), and the area of the indicator diagram be taken as independent of the shape of its ends.

CHAPTER II.

THE PHASE RULE.

Equilibrium. Equilibrium of phases. The phase rule. Non-variant systems. Monovariant systems. Divariant systems. Other systems. The principle of latent heat. Application of the phase rule. One component. Labile equilibrium. Allotropic solids.

Equilibrium.

In studying the qualitative conditions of equilibrium for substances in contact with their saturated solutions, the detailed examination of a system consisting of a solid in contact with its own liquid and vapour is in the first place expedient. The results can then be extended to the more complex conditions introduced by the presence of a second substance. Both are cases of true equilibrium.

Let us consider the single substance water. It can exist in three phases, the solid, the liquid and the vapour. A system containing two or more of these phases in equilibrium is still said to consist of a single independent component, namely, water, because the total mass of water being constant, the relative amounts of the phases are dependent on each other. For if, by changing the external conditions of temperature or pressure we increase or diminish the amount of liquid, we shall necessarily diminish or increase simultaneously the amount of one at least of the other phases.

In a mixture of salt and water, the amounts of the salt and of the water are not mutually dependent—decreasing the quantity of salt does not correspondingly increase the quantity

of water. They are independent variables of the system, and each of them is a distinct component. Here again, we can have only one gaseous phase, and only one liquid phase; for, when equilibrium is reached, the compositions of both vapour and liquid are homogeneous throughout. But we can have ice and crystals of salt, the latter in some cases being present in both hydrated and anhydrous forms. The number of solid phases is therefore only limited by the nature of the salt.

Another case arises in the reaction between lime and carbon dioxide to form calcium carbonate, which is represented by the reversible chemical equation

$$CaO + CO_2 \rightleftharpoons CaO.CO_2.$$

The total quantity of CaO both free and combined does not depend on the quantity of CO_2 present; they are independent variables, and therefore components of the system. But the amount of $CaCO_3$ does depend on the amount of lime and carbon dioxide, for if we decompose $CaCO_3$ more of these substances is found. Thus $CaCO_3$ is not a component, but merely a solid phase in which the two components happen to exist in a definite proportion. A component in this sense need not be a chemical compound, though it usually is so, and, on the other hand, each compound is not necessarily a component. Again, the number of components in the same material system may change with the physical conditions, as in the case of the system

$$2H_2 + O_2 = 2H_2O,$$

at high and at low temperatures.

We are thus led to define:

(i) A phase as a mass chemically and physically homogeneous, or, as a mass of uniform concentration.

(ii) The components of a phase or system, as the substances contained in it which are of independently variable concentration.

Equilibrium of phases.

We saw in the introductory chapter that, to attain equilibrium in an isothermal system, it is necessary that either the thermodynamic potential at constant volume ψ or the thermodynamic potential at constant pressure ζ should be a minimum. These thermodynamic

potentials will depend not only on θ and p, or θ and v respectively, but also on the composition of the phases. Let us imagine that we have a homogeneous phase containing n components, and that we increase one of these components by a small mass δm. The consequent rate of change of the ψ function is given by the partial differential coefficient $\partial\psi/\partial m$, which measures the change in ψ per unit mass of the component added to the phase. This function, $\partial\psi/\partial m$ or μ, is, as we have said, called by Gibbs the chemical potential or the potential of the component in the given phase. It is equal to the work required to increase by unity the amount of that component by means of a reversible process, under the conditions of constant temperature and volume.

If we have several phases in contact with each other, any of the components may pass from one phase to the other. For instance, if solid $CaO . CO_2$ is in contact with gaseous CO_2 and solid CaO, some CO_2 may pass from the gaseous to the solid phase, and, at the same time, some CaO will pass from one solid phase to the other.

In such a case the work done per unit change will be written

$$\frac{\partial\psi_2}{\partial m} - \frac{\partial\psi_1}{\partial m} \text{ or } \mu_2 - \mu_1.$$

If this potential difference is negative, the component will pass from the phase 1 to the phase 2; and *vice versâ*. If the potential difference is zero, there will be equilibrium.

Thus the condition of general equilibrium is that the chemical potential of each component must have the same value in each phase in which the component is present.

If the system is maintained at constant temperature and pressure, instead of at constant temperature and volume, the same reasoning can be applied to the ζ function, and a similar condition of equilibrium will hold with respect to the corresponding chemical potential.

The phase rule.

Let us now take the case of the equilibrium of r phases containing n components. In order to fix the composition of unit mass of each phase we must know the amounts of $n-1$ components which are contained

UNIVERSITY OF CALIFORNIA

in it. The amount of the last component is then also known. In the composition of each phase there are $n-1$ variables, and, since there are r phases, the number of variables, due to this cause, in the whole system is $r(n-1)$. But, beside the compositions, the temperature and the pressure can also vary independently. Thus the total number of variables in the system is

$$2 + r(n-1).$$

In order to determine these variables, we must find equations between them. The potentials of the components are functions of the temperature, pressure and the composition of the phases, and will therefore give us the equations that we require. Now, as we have seen, the potential of each component in every phase must be equal and no other condition is necessary for equilibrium. Therefore, for each component, we shall have $r-1$ equations, or, for all the components,

$$n(r-1) \text{ equations.}$$

The excess of the number of variables over the number of equations is thus

$$2 + r(n-1) - n(r-1) = n + 2 - r,$$

and this must therefore represent the number F of degrees of freedom of the system, or

$$F = n + 2 - r.$$

This equation is the expression of the Phase Rule, a generalization which we owe to Willard Gibbs[1].

Non-variant systems.

If the number of phases in equilibrium with each other is two more than the number of components, or

$$r = n + 2,$$

the number of degrees of freedom becomes zero, that is, the system is completely determined, and is therefore called a non-variant system.

For example, if three phases of water can be obtained in

[1] *Trans. Conn. Acad.* vols. II. and III., 1875–8, translated *Thermodynamische Studien*, Leipzig, 1892, and *de l'Equilibre des Systèmes Chimiques*, Paris, 1899.

equilibrium, the whole system is perfectly definite. Each phase must have a definite concentration, and the temperature and pressure each a definite value. That this is indeed the case, is a matter of experimental knowledge. Ice, water and steam can exist together in equilibrium at one temperature and pressure only. The usual freezing point of water is the temperature at which ice and water can permanently coexist under the normal atmospheric pressure. But when we have ice, water and steam isolated in a closed vessel, the pressure is that of the water vapour only, and in the neighbourhood of the freezing point this pressure is about 4·7 mm. of mercury. The freezing point of water is lowered by 0°·007 centigrade for each additional atmosphere of pressure, so that reducing the pressure from 760 mm. to 4·7 mm. will raise the freezing point by approximately that amount. We find that ice, water and steam can co-exist in permanent equilibrium only at a temperature of + 0°·007 and at a pressure of about 4·7 mm. of mercury. If either temperature or pressure be changed and kept at its new value, one or other of these three phases must eventually disappear. Thus, on raising the pressure, the vapour will all condense; on lowering it, water and ice will evaporate and finally ice will be left in equilibrium with vapour at the slightly lower temperature corresponding to the new pressure.

Monovariant systems.

If the number of coexistent phases is $n + 1$, i.e. one more than the number of components, the system ceases to be non-variant. To determine all the variables involved, it will be necessary to arbitrarily fix one of them. In our typical case of water, if we have only liquid and vapour in equilibrium with each other, an infinite series of temperatures and pressures are possible; but, for each definite temperature, at one definite pressure, and at that pressure alone, is equilibrium attained.

Divariant systems.

When the number of phases in equilibrium is n, so that it is equal to the number of components, we must arbitrarily fix two variables before the system is determined. A divariant system with two degrees of freedom

is then obtained. Our example in the case of water is now one phase alone, let us say the vapour. A gas or non-saturated vapour can possess any temperature at any pressure, and it is only when both these data are chosen that the other variable, the concentration, is determined.

Other systems.

In the case of one component, there must at least be an equal number of phases, but with more than one component it is possible to have cases in which a smaller number of phases, $n-1$, $n-2$, etc., is concerned. Such systems would be trivariant, tetravariant, etc., but they are too complicated to be of much present interest or importance.

The foregoing paragraphs give a statement of Willard Gibbs' Phase Rule. It will be noticed that nothing is said about the possibility of the existence of non-variant systems with more than $n+2$ phases in equilibrium. Since, however, the system must be definitely determined by $n+2$ phases, it is improbable that a greater number would coexist, and, as far as is known to the writer, none have been described, except those involving false equilibrium, maintained by passive resistance to change which is the analogue of frictional force.

Again, the Phase Rule implies that the phases involved are homogeneous throughout. This excludes the consideration of disturbing factors such as gravity, which makes the lower layers of a gas or solution more concentrated than the upper ones, or surface tension, which differentiates the free surface layer from the bulk of a solid or liquid. Such effects are, however, usually unimportant.

The latent heat equation.

Hitherto we have considered equilibrium only, and have not taken into account the phenomena which accompany a change in one of the conditions. The relations governing such changes can be deduced from the latent heat equation

$$\frac{dp}{d\theta} = \frac{\lambda}{\theta(v_2 - v_1)},$$

obtained on p. 29, in which λ and v refer to molecular quantities of the working substance. Let us take, as an example of its application, the equilibrium between a liquid and its vapour. If both λ and $v_2 - v_1$ are positive, a rise in the temperature will, as we have seen, cause a rise in the pressure also. This means that more liquid evaporates, and λ being positive, this evaporation absorbs heat, and thus cools the system.

On the other hand, a rise in the pressure produced by a compression of the vapour will obviously cause condensation; λ being positive, heat is evolved, and the temperature of the system rises till a new equilibrium is reached.

Let us now take a case in which $v_2 - v_1$, and therefore $dp/d\theta$, is negative, for example: a mass of water and ice in equilibrium at the freezing point, under the pressure of the walls of an elastic vessel. The addition of heat causes ice to melt and the combined volume of the liquid and solid to contract. This causes the pressure to fall, and since $dp/d\theta$ is negative, the freezing point will rise and a new equilibrium be reached.

Thus in each case a change in the external conditions causes compensating changes within the system.

This principle, originally due to James Thomson, was developed in various directions about the year 1850 by William Thomson (Lord Kelvin), Rankine and Clausius. In recent times Le Chatelier has been prominent in illustrating its application to chemical systems, the reversible and therefore thermodynamic character of which has been clearly realized only since the work of Gibbs and Van't Hoff.

These two principles, the Phase Rule and the theorem of latent heat, furnish a means of tracing all the qualitative phenomena of physical and chemical equilibrium. They involve no knowledge of the nature of matter or of the reactions which occur, and no distinction is drawn between physical and chemical changes. The Phase Rule is concerned merely with the relative number of components and coexistent phases, and the theorem of latent heat needs for its application only an experimental knowledge of changes of density and concentration, and the corresponding thermal phenomena.

Application of the phase rule—one component.

When systems of one component are studied in detail, it is convenient to represent the relations involved on a diagram. Thus Figs. 8—11 illustrate qualitatively the phenomena which we have already briefly described as characteristic of water substance. The curves are diagrammatic, and are not drawn to scale.

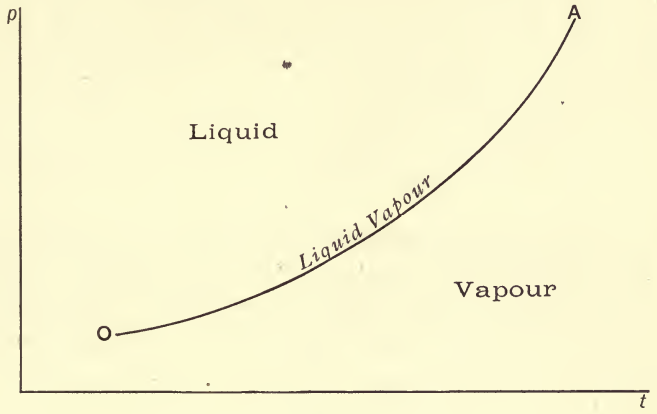


Fig. 8.

The curve *OA* traces the connection between the temperature and the vapour pressure when a mass of water is in equilibrium with its own vapour. This curve divides the diagram into two areas. A mass of water substance the temperature and pressure of which are represented by any point in the space lying below *OA* must exist in the state of unsaturated vapour, and can none of it be liquid. Above *OA* the position of every point represents conditions of temperature and pressure which can exist only when all the substance is liquid. Thus the area below *OA* represents unsaturated vapour, and the area above *OA*, more or less compressed liquid, and along the line *OA* alone can there be liquid and vapour in equilibrium.

If the temperature sinks below the freezing point and ice forms, the liquid will disappear and a curve *OB*, giving the vapour pressure of ice, can be traced a few degrees below the freezing point. This curve is not continuous with *OA*, for more heat is required to evaporate a gram of ice than a gram

of water, and our thermodynamic equation therefore shows that the rate of change of pressure with temperature, that is,

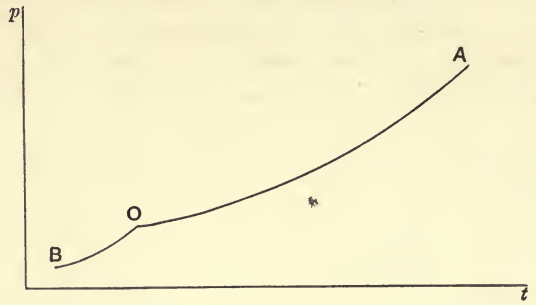


Fig. 9.

the slope of the curve, is greater for the solid than for the liquid. At the freezing point, however, the vapour pressures of solid and liquid have the same value, for otherwise transformation of one phase into the other would occur, and equilibrium be impossible.

Like *OA*, the curve *OB* divides the diagram into areas representing two phases, in this case solid and vapour, which can be in equilibrium only along the dividing line. If the

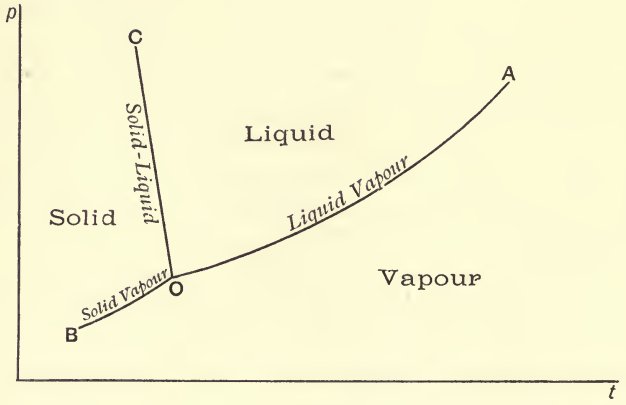


Fig. 10.

system be compressed at the freezing point, the vapour disappears, and solid and liquid remain together in equilibrium.

If the pressure be raised, as we have seen, the freezing point is lowered, and therefore the equilibrium curve is one which, springing from *O*, runs upward with a slight inclination towards the axis of pressure. The latent heat equation shows that this is related to the fact that the volume becomes smaller on fusion. In substances, such as naphthalene, etc., where fusion causes expansion, the slope of the fusion curve is in the other direction.

All these monovariant curves start from the point *O*. Their other limits have now to be considered. *OA*, the liquid-vapour curve, obviously ends at the critical point, where the distinction between liquid and vapour is lost. *OB*, the solid-vapour curve, has only been experimentally traced a few degrees below the freezing point of water, but there seems some ground for believing that the vapour pressure of the solid never quite vanishes, though it diminishes as the temperature sinks towards the absolute zero. The solid-liquid curve, *OC*, will be considered below; the effect of high pressure is usually to make the properties of solids resemble those characteristic of liquids. This is indicated by experiments of Spring[1], who found that metals subjected to a pressure of several thousand atmospheres assumed a structure similar to that possessed by them after fusion.

The point *O*, at which the three curves meet, represents a non-variant system. With only one component present it is always, as here, a triple point; but the number of curves which must meet in order to constitute a non-variant equilibrium will increase by one for each new component. Such points as *O* are termed non-variant, transition or inversion points. The first name we have explained; the second and third express the fact that it is at these points alone that unlimited conversion from one phase into another can occur without change of temperature.

Each of the curves *OA*, *OB*, *OC* represent equilibrium between two phases, i.e. for monovariant systems. Along them, if one variable, temperature or pressure, be chosen, the other is at once determined and can have only one value. They are the boundary curves for the areas *AOC*, *COB* and *BOA*. The

[1] *Rapports Congrès de Physique*, Paris 1900, I. 402.

curve *OA* is a liquid-vapour curve, *OB* is a solid-vapour curve, and *OC* a solid-liquid curve. Thus under the conditions of temperature and pressure represented by any point in the area *AOC* the substance will exist in the state of liquid, at points in *COB* in the state of solid, and in *BOA* in the state of vapour. In order to determine the position of a point in any one of these areas, two independent variables must be fixed; the points in these areas represent divariant systems.

Labile equilibrium.

Under normal conditions the three phases cannot exist singly except under the temperatures and pressures represented by points inside their corresponding areas; but, as is well known, by preventing all disturbance a liquid can often, in the absence of its solid phase, be cooled considerably below its proper freezing point without solidification. Vapour, too, can, in the absence of liquid or dust nuclei, be cooled or compressed till it becomes supersaturated. Such cases are examples of substances in what is known as a *labile* or *metastable* state, and only occur in the absence of one of the phases whose equilibrium is represented by the boundary which has been passed. The curves of our diagram, for instance, illustrate the equilibrium between two phases. If one of these phases be not present, the conditions are entirely altered; the initial formation of one of the phases is a different process, governed by different conditions, of which surface energy is one of the most important. By cooling water carefully, therefore, the vapour pressure curve can be traced below the freezing point, and experimentally proved to lie above the corresponding curve for ice. It is indicated by the dotted line *OD* in the diagram.

If we begin with unsaturated vapour only, we have a divariant system indicated by some point on our diagram such as *H*. Cooling the vapour will cause a change of pressure depending on the nature of the substance. Let us take the system along some path represented by the arbitrary curve *HKL*. Eventually saturation is reached and the curve *HK* cuts the liquid-vapour curve at *K*. If no nuclei are present, however, cooling can take place without condensation and the

curve can be traced from K to L. The phenomena of supersaturation have been studied in the case of water vapour by

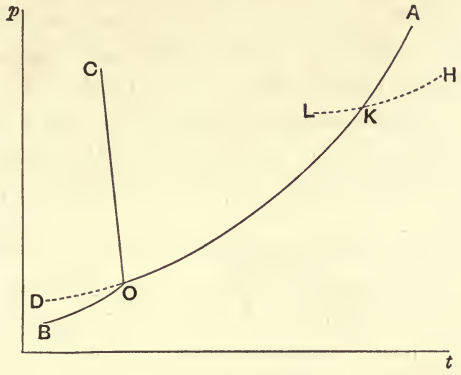


Fig. 11.

Aitken[1] and C. T. R. Wilson[2]. Aitken showed that air, carefully freed from dust by passage through cotton wool, could easily be cooled below its normal temperature of saturation without formation of moisture, and Wilson has found that the electric ions produced in air by the passage of Röntgen rays, by the incidence of ultra-violet light on a negatively electrified zinc plate, and by other methods, act as condensation nuclei like dust particles. The degree of supersaturation necessary for condensation is greater in the case of the ions than for dust particles, and greater for positive than for negative ions.

These phenomena are closely connected with the surface tension between the liquid which would be formed and the substance surrounding it. The surface tension shows that a drop of liquid has, in addition to its mass energy, an amount of free superficial energy proportional to the area of contact between it and the air. Since the free energy tends to a minimum, a given volume of liquid will, other things being equal, assume the state which gives the minimum surface. The larger drops in a space saturated with water vapour will therefore grow at the expense of the smaller ones, by means of

[1] *Trans. R. S. Ed.* xxx. 337, 1881 *et seq.*

[2] *Phil. Trans. A.* vol. cxcii. p. 403, 1899 and cxciii. p. 289, 1899.

evaporation from the more convex surfaces where, as we shall see in a later chapter, the vapour pressure is higher, and condensation on the less convex surfaces where it is lower. The precipitation of the excess of water from a supersaturated space, in the absence of dust or other nuclei, can only begin by the formation of very minute drops. The total area of these will be very large in proportion to their volume, and consequently the change might involve an increase in the total free energy of the system. When this is the case, spontaneous precipitation cannot occur.

Similar cases of supersaturation are found in liquids, which can often be cooled far below the melting points of their solids, and still remain in the liquid state. If a crystal of the solid be then introduced, crystallization of the whole mass will usually at once occur. This subject has been extensively studied by Tammann[1], who finds that the power of spontaneous crystallization, as measured by the number of centres of crystallization started in unit time, increases to a maximum after the temperature sinks below the melting point, and then diminishes again rapidly as the surfused liquid is further cooled. The velocity with which the crystals grow when once in existence has no relation to this power of starting the process, and is generally at a maximum at a very much higher temperature. When the surfused liquid is cooled much below the melting point, the power of spontaneous crystallization and the rate of growth both become so small that the liquid remains for an indefinite time in the surfused condition. Its viscosity also increases at an enormous rate, and finally the surfused system passes into the state in which it is called an amorphous solid. Thus, an amorphous solid, or a glass as it is often called, seems really to be an under-cooled liquid, and not a solid at all.

Probably, in this case also, the surface tension between the crystals and the liquid surrounding them is one of the factors which cause supersaturation to occur. The case is not quite analogous to that considered above, in which drops of water

[1] *Zeits. phys. Chem.* XXI, 17, 1897. *Wied. Ann.* LXII, 28, 1897; LXVI, 473, 1898; LXVIII, 553 and 629, 1899. *Ann. der Physik*, I, 275; II, 1, 1900. See also an abstract in the *Rapports prés. au Congrès de Phys.*, Paris, 1900, I. 449.

are surrounded by their vapour, for the surfaces of crystals are plane and not curved, so that there is nothing of the nature of an increased pressure due to curvature inside them. Some suggestions on this subject have been made by Gibbs[1], who points out that, on a dynamical view of the equilibrium between a crystal and the surrounding liquid, there need not necessarily be the same exact conditions of equilibrium between them as there are between a liquid and its saturated vapour. The equilibrium between a liquid and its vapour is explained as an equality between the number of particles evaporated and condensed in unit time, and, since the quantity of liquid can increase or diminish by infinitesimal amounts, the slightest change in the rates of evaporation or condensation, caused by the least variation in the temperature or pressure, is enough to alter the equilibrium. But in order that a crystal should increase in size, a whole new layer must be deposited on its faces, and therefore the thermodynamic potential of the liquid phase required for the growth of a crystal probably exceeds by a finite quantity that needed for its solution. At the edges of a crystal, however, the particles are probably less firmly held, and an exact balance of opposite processes may there occur.

Phenomena analogous to those of the surfusion of pure liquids and of the growth of crystals in them will be found in solutions of one substance dissolved in another (two component systems), and a case similar to the condensation of vapour by gaseous ions will be found in the coagulation of colloidal solutions by the addition of electrolytes.

Allotropic solids.

When the solid can exist in more than one crystalline form we get more complicated phenomena, though here also the non-variant systems are represented by triple points. Thus Fig. 12 shows the equilibria in the case of sulphur, which, as is well known, is found both as monoclinic and rhombic crystals. The melting point of the monoclinic sulphur is 120° and its density 1·96, while the corresponding numbers for the rhombic variety are 114°·5 and

[1] *Trans. Connect. Acad.* III, 494, 1874–1878.

2·05. Since the densities are different, it is easy to observe the temperature at which one modification passes into the

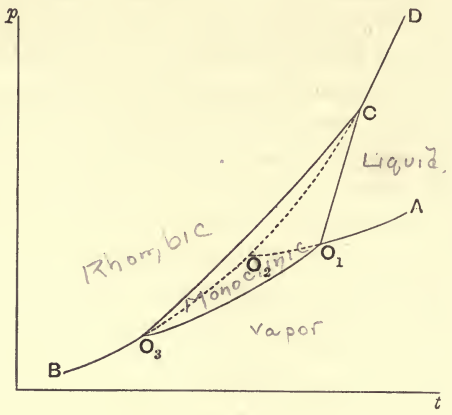


Fig. 12.

other by means of a dilatometer, and Reicher[1] has shown that the temperature of conversion is 95°·6. The change is a very slow one, hence the possibility of measuring the melting point of the rhombic crystals at 114°·5, though they are of course in an unstable condition. We thus have three points on our diagram; $O_1(t=120°)$ at which liquid, vapour and monoclinic solid are in equilibrium, $O_2(t=114°{\cdot}5)$ the unstable meeting point of liquid, vapour and rhombic solid, and $O_3(t=95°{\cdot}4)$, where the two solids and the vapour coexist. Starting from O_1 is O_1A, the liquid-vapour curve, giving the relation between temperature and the vapour pressure of the liquid, O_1C the curve showing the variation of the fusion point of monoclinic sulphur with the pressure, and O_1O_3 giving the equilibrium between monoclinic sulphur and its vapour. Below O_3 rhombic sulphur has the smaller vapour pressure, and is, therefore, the stable form. Thus starting from O_3 besides O_3O_1 we have the stable curves O_3B, the vapour pressure curve of the rhombic solid, and O_3C showing the relation between the pressure and the transition point between the two forms of solid. The pitch of this curve has been determined by Reicher, and Roozeboom

[1] Van 't Hoff-Cohen, *Studien zur Chemischen Dynamik*, 1896, p. 185.

has calculated the position of C, at which the two curves O_3C and O_1C must meet if no other modification of sulphur exists, to be about 135° and 400 atmospheres. Here, the two solids would be in equilibrium with the liquid, and at higher pressures the less dense monoclinic sulphur would disappear and some curve such as CD would express the monovariant system rhombic solid and liquid. This curve would, if continued downwards, be continuous with the unstable curve CO_2.

Thus neglecting labile equilibria, which are not completely described by the Phase Rule, we have three non-variant points O_1, O_3 and C, at each of which three curves meet, each curve representing the series of states of a monovariant system. Moreover, as in the case of water, the areas of the diagram represent the states of divariant systems composed of one phase only. Thus the area below AO_1O_3B represents the vapour, the area to the right of AO_1CD the liquid, the area to the left of BO_3CD the rhombic solid, and the area enclosed by CO_1O_3 the monoclinic solid. Outside its characteristic area each phase can exist only in a labile and unstable state.

An interesting case of allotropy has recently been discovered by Tammann[1], who finds that at low temperatures with very high pressures two new crystalline varieties of ice exist, both of which are denser than water. He has also traced parts of the curves giving the conditions of equilibrium between the three solid phases.

Some solids are said to exist in allotropic forms one of which is amorphous. But, as pointed out by Lehmann in his *Molekularphysik* and confirmed by Tammann's work described above, amorphous bodies are probably surfused liquids. It seems likely (1) that a true solid is always crystalline, and (2) that the temperature and pressure necessary for its stability have definite limits on all sides. Thus the curve OC in Fig. 10, instead of ending at a critical point where solid and liquid become indistinguishable, bends to the left and eventually cuts the curve OB. It then incloses a definite area within which alone the conditions allow the permanent existence of the crystalline phase.

[1] *Ann. der Phys.* II. 1, 1900, also *Paris Reports*, 1900.

CHAPTER III.

THE PHASE RULE. TWO COMPONENTS. SOLUTIONS.

Compounds, mixtures and solutions. Anhydrous solutes. Hydrated solids. Concentration curves. Two liquid components. Alloys. Solid solutions. Two volatile components. Three components. The problems of solution.

A PHASE consisting of two or more components may be a mixture, a solution, or a compound. If it is constituted according to the theorems of definite and multiple proportions it is a *compound*; if the relative quantities of the components can vary continuously between certain limits it is either a *solution* or a *mixture*. The distinction between the two latter is not sharp; though when the properties of the resultant are sensibly the sum of those of the components, as is nearly true for gases, it is usual to class it as a mixture.

Compounds, mixtures and solutions.

Solutions as thus defined need not necessarily be liquids. In so far as gases fail to conform to Dalton's law, mixtures of them must be treated as solutions, while instances of solid solutions are found in the alloys, the mixed alums, glasses, and perhaps in the substances formed when hydrogen and other gases are absorbed by metals. These cases will be considered more fully later.

Two components which form a solution may be soluble in each other in all proportions, when they are called *consolute*, or only to a limited extent. In the latter case it is customary to

distinguish between the medium or *solvent*, and the dissolved substance or *solute*. This phraseology, however, though convenient, is of no import from the point of view of the Phase Rule, which draws no distinction in kind between the two components involved in an equilibrium.

For the general case of the equilibrium of two components, when any disturbing effects of surface tension, gravity, electrification etc., can be neglected, the Phase Rule shows us that we must assemble four coexisting phases to get a non-variant, three for a monovariant and two for a divariant system. Thus in the case of sodium chloride and water, the system containing salt, ice, solution and vapour can exist at one temperature and pressure only—at the freezing point ($-22°$ C.) of a saturated solution under the pressure of its own vapour. If heat be applied, the solids will eventually disappear, and conversely, if heat be taken away, the whole of the liquid will freeze; but the temperature, pressure and concentration will remain constant throughout. Such a constancy used to be considered as the characteristic of a pure chemical compound, and these mixtures of salt and ice with constant melting points were termed cryohydrates by Guthrie[1]. Considered in the light of the Phase Rule, however, it is clear from the constancy of the melting point that four phases must be present, i.e. that two different solids must separate, and therefore that the solid phase is not a chemical compound, but a conglomerate of two solids. It is obvious that the cryohydric point is the lowest temperature which can be reached when the salt is used with ice as a freezing mixture, and thus, when a low temperature is required, a salt having a low cryohydric point must be used. Calcium chloride, for instance, gives a non-variant point at about $-55°$, where the hydrate, ice, solution and vapour are in equilibrium.

Graphic representation of two component systems.

In passing from systems of one component to those of two, we introduce a new variable, namely, the composition of each phase. The obvious way to represent this diagrammatically is to use a solid construction, the percentage composition of a variable phase

[1] *Phil. Mag.* (4) XLIX. (1875); (5) I. and II. (1876); VI. (1878).

being measured along an axis at right angles to the plane of the paper, the pressure and temperature axes being used in that plane. The state of the system will now be represented by a point in space, fixed by three co-ordinates. The trivariant systems are represented by volumes, the divariant by the surfaces separating those volumes, the monovariant by the lines in which the surfaces cut each other, and the non-variant by the points of intersection of the lines.

For convenience, however, it is usual to represent these three dimensional diagrams by plane figures. In examining such figures it should always be borne in mind that they are only suggestions of solid diagrams, and that the lines seen in them do not in general really lie in one plane.

Anhydrous solutes.

The simplest cases of two component systems are furnished by solids which cannot crystallize in combination with the solvent, such as the anhydrous salts and water. Here we have a quadruple transition point, of definite pressure, temperature and concentration of solution, at which solid salt, ice, saturated solution and vapour are in equilibrium in any proportions. This point is shown by *O* in Fig. 13—a diagrammatic sketch of the solid figure, in which the composition of the liquid phase is taken as the third axis.

Leaving the transition point *O* by the addition of heat, we can, if salt be present in excess of ice, advance along the curve *OA*, which represents the monovariant system salt, solution and vapour. It resembles the corresponding curve of our former diagram, except that instead of showing the vapour pressure of a pure substance, it represents that of a solution, saturated with salt at each temperature. Since the presence of salt lowers the vapour pressure of a liquid, this curve lies below that for the pure solvent, unless the solute itself be volatile to an appreciable extent, a case which will be considered later. When the solubility increases with the temperature, the curve *OA* will also rise less steeply than that for the pure solvent, for the lowering of vapour pressure due to the solute will constantly increase. The curve will end at a critical point for the solution,

at which the solid may melt and either give another quadruple point or mix perfectly with the solution. Another possibility is that by decreased solubility or increased vapour pressure the liquid and vapour may come to have the same composition.

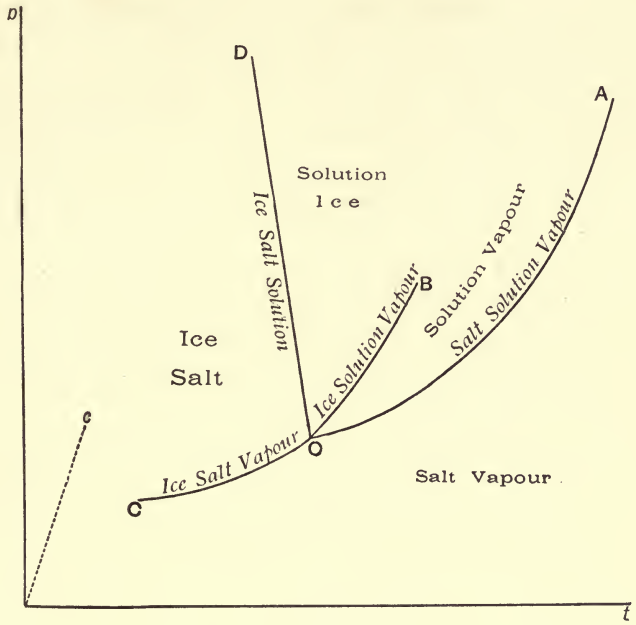


Fig. 13.

Again returning to the quadruple point *O* on Fig. 13 let ice, instead of salt, be present in excess. The addition of heat causes ice to melt and thus solvent to be formed and salt dissolved. This proceeds at a constant temperature till all the salt is dissolved. A further supply of heat melts more ice, and now the solvent formed from it dilutes the solution, which therefore ceases to be saturated. As long as ice remains, we have an equilibrium between it and an unsaturated solution, that is, we advance along a curve, giving the freezing points of solutions of constantly decreasing concentration, ending at *B*, the freezing point of the pure solvent, when the amount of ice which has been melted is enough to make the concentration of

the solution negligible. From the point B may be drawn the same liquid-vapour and liquid-solid curves which we drew for our one component system.

The more important properties of the solubility curve OA, and the fusion curve OB, are those represented by their projections on the temperature-concentration plane, the relations connecting pressure with temperature, best seen in our present diagrams, not being usually so prominent.

Let us now again consider the non-variant system represented by O. Taking away heat, we shall freeze the whole of the liquid, and obtain the monovariant system salt, ice and vapour. For each temperature there is a definite vapour pressure, and we get a curve such as OC on the diagram.

Once more starting from O, we can by increase of pressure condense all the vapour and obtain the last possible monovariant combination; that of salt, ice and saturated solution. The direction of this curve depends on the relative volumes of the salt and ice when solid and when forming a saturated solution, and on the signs of the heats of solution and fusion. Knowing these, the direction of the curve could be calculated from our equation; but little has been done towards tracing it experimentally.

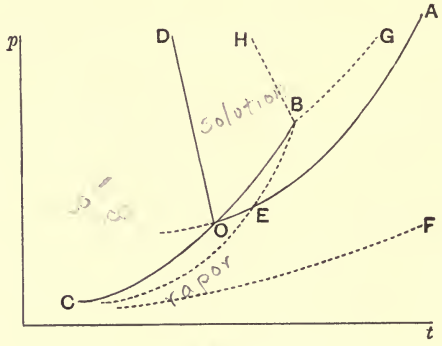


Fig. 14.

As before, the areas of the figure represent divariant systems, although in this case each of these systems consists of two phases. A reference to Fig. 13 will show the pairs of

phases which can exist in the different areas, and the meaning of the curves along which alone can three phases be in equilibrium.

If the solute is appreciably volatile as well as the solvent, we must add to our diagram *CF*, giving the vapour pressure of the pure solute, and *CEB* the vapour pressure of the pure ice, which will now not coincide with *OC*, the vapour pressure curve for the mixed solids. To complete the figure we may draw also *BG* the liquid-vapour curve, and *BH* the solid-liquid curve for the pure solvent. If the solute were very volatile it would be possible for the curves *OA* and *BG* to cross each other, that is, for the vapour pressure of a saturated solution to be higher than that of the pure solvent.

Hydrated solids.

It is well known that many salts crystallize from solution in combination with one or more molecules of water, forming solids which are called hydrates. It is possible also for solute and solvent to freeze out together in the form of a solid solution in which the proportions need not be related to those of the chemical equivalent weights. In either case our diagrams become more complicated, for each possible solid phase will have to be considered.

Fig. 15 illustrates a case such as that of sodium sulphate, which usually crystallizes from water as $Na_2SO_4 . 10\,H_2O$. The crystals melt at 32°·6 and pass into the anhydrous salt and water. Another hydrate, $Na_2SO_4 . 7\,H_2O$ can be obtained by adding alcohol to the solution in water, but it is unstable with respect to both the anhydrous salt and the other hydrate, and need not here be considered.

The quadruple point *O* represents a non-variant system in which ice, hydrate, saturated solution and vapour are in equilibrium. The monovariant curves springing from it are similar to those considered in the case of the anhydrous salt, and need not detain us. When, however, we heat the system composed of hydrate, solution and vapour, the anhydrous salt appears as a new solid at *P*, and another non-variant system is formed at a temperature of 32°·6 and a pressure of 30·8 mm. of mercury[1].

[1] Cohen, *Zeits. f. physikal. Chemie*, XIV. 90, 1894.

From this point P we can pass along PA, the monovariant curve representing salt, solution and vapour; along PD_1 representing hydrate, salt and solution; along PO representing

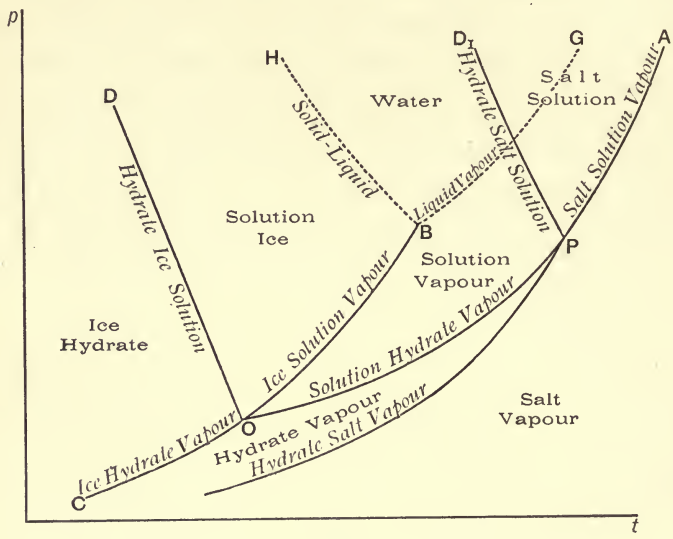


Fig. 15.

hydrate, solution and vapour; or along the new curve PC representing the equilibrium between hydrate, salt and vapour. This latter can be realized experimentally by increasing the volume, or passing a current of air over the non-variant system, till all the solution has disappeared. The crystals of hydrate then "effloresce" as it is called, and give a definite vapour pressure for each temperature. In the case of sodium sulphate the vapour pressure of the anhydrous salt is inappreciable; but, in the general case, the curve gives the sum of the vapour pressures of the constituents. The curve PC cannot lie above PO; for if the vapour pressure of the effloresing hydrate were greater than that of the saturated solution at the same temperature, the hydrate would always be converted into solution, and this does not occur. For some systems the curves lie well apart, for others they seem nearly to coincide. Thus at 20° the vapour pressures of solution and hydrate are for calcium chloride 5·4 and 2·3, for

sodium carbonate 16·0 and 10·1, for sodium sulphate 15·7 and 13·9, for cadmium bromide 10·0 and 9·0, and for barium iodide 8·4 and 8·4.

Concentration curves.

Hitherto, we have considered the qualitative phenomena only, and no attempt has been made to draw the diagrams to scale. For the quantitative study of a monovariant system the general sketch of the solid model which has hitherto been used is conveniently replaced by a projection of the monovariant curve in question on one or other of the three planes, according to the pair of variables to be examined. Experiments on the relation between temperature and solubility are illustrated by projecting the curve OA (Fig. 13) on the c-t plane. The pressure at each point should be that of the vapour, but, since the solubility of a solid does not change much with pressure, measurements under constant atmospheric pressure practically give the theoretical monovariant curve. As before, the regions on each side of the curves represent the states of different systems, the curves themselves giving the conditions of equilibrium between them.

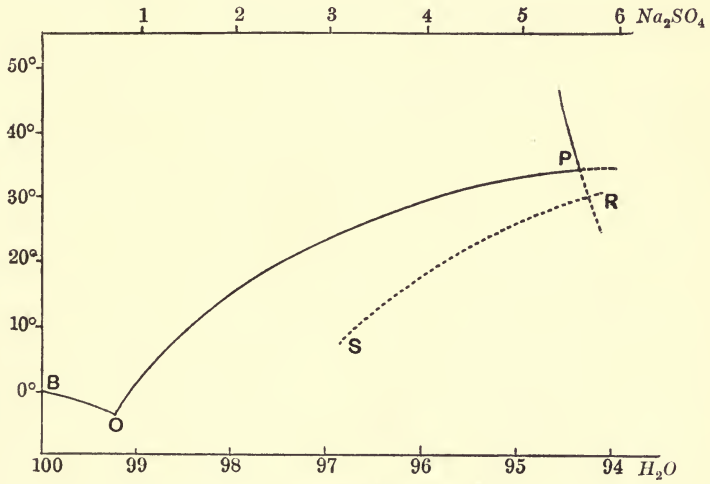


Fig. 16.

Thus Fig. 16 gives our quantitative knowledge of the equilibrium of sodium sulphate and water in this way, the

pressure throughout being taken as constant. The lettering is the same as that of the general diagram in Fig. 15. Thus *O* is the cryohydric point, and *OB* the fusion curve, showing the gradual rise in the freezing point as the amount of salt diminishes. *OP* is the solubility curve of the hydrate $Na_2SO_4 . 10\,H_2O$. When the temperature reaches 32°·6 and about 6 molecular per cents. of Na_2SO_4 are dissolved in 94 of water, the second non-variant point is reached, and the anhydrous salt appears. Beyond this temperature the measured solubility is that of the anhydrous salt, which, for some distance at all events, decreases with rising temperature, and has, therefore, a negative heat of precipitation. The solubility of the other hydrate $Na_2SO_4 . 7\,H_2O$ is represented by the dotted curve *RS*; solutions saturated with respect to this

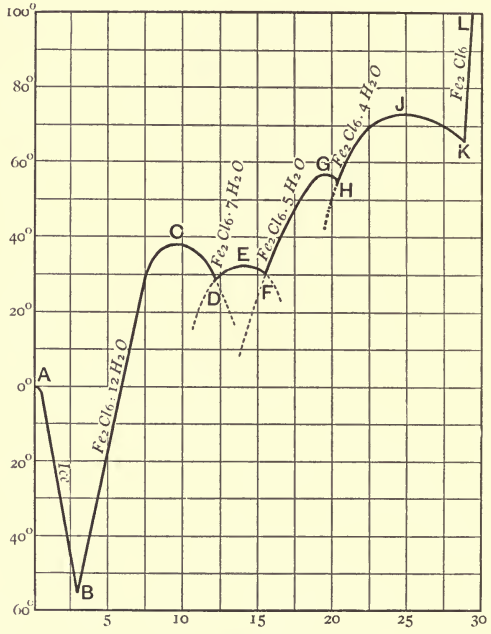


Fig. 17.

hydrate are thus supersaturated with respect to the other, which will, therefore, crystallize out when a fragment of its

solid is dropped in. Sodium sulphate has only one stable hydrate, but many salts can form several. Among these, calcium chloride and ferric chloride have been studied in detail by Roozeboom[1]. His results for ferric chloride are illustrated by Fig. 17. There are four hydrates, containing twelve, seven, five and four molecules of water, which with the anhydrous salt and ice make six possible solid phases. *AB* is the fusion curve giving the freezing points of solutions of concentrations varying from nothing at *A* to that of the cryohydrate of $Fe_2Cl_6 . 12\,H_2O$ at *B*. The cryohydric temperature is $-55°$, and here we have a non-variant system, consisting of ice, the hydrate, saturated solution and vapour. From *B* onwards runs the solubility curve of this hydrate, and at *C*, where the curve shows a maximum, the solution has the same composition as the hydrate, which can, therefore, completely melt without change of temperature. Beyond *C* the liquid can take up more salt, and the solution contains more ferric chloride than the crystals. Thus *C* represents the melting point of the hydrate, 37°, the curve *CB* shows the lowering of melting point caused by the addition of water, and *CD* that due to the addition of ferric chloride. It is important to notice this similar effect of changing the composition of a system in opposite directions on the two sides of a definite compound. At *D*, 27°·4, a new hydrate, $Fe_2Cl_6 . 7\,H_2O$, appears. This hydrate was actually discovered by Roozeboom from a study of the solubility curves. Its melting point, *E*, is 32°·5.

In a similar way the curve *FGH*, between 30° and 55°, belongs to the hydrate $Fe_2Cl_6 . 5\,H_2O$, and the curve *HJK* to the hydrate $Fe_2Cl_6 . 4\,H_2O$ which melts at *J*, 73°·5. At *K*, 66°, begins the solubility curve of the anhydrous salt.

In the light of this diagram let us trace the behaviour of a solution of ferric chloride which is evaporated to dryness at a constant temperature of 31°. The phenomena will be represented by a horizontal straight line across the diagram. When the curve *BC* is reached, $Fe_2Cl_6 . 12\,H_2O$ separates out, and the solution solidifies. Further removal of water will cause first liquefaction, and then re-solidification to $Fe_2Cl_6 . 7\,H_2O$ when *DE* is cut. Again, the solid will liquefy, and again become solid

[1] *Zeits. phys. Chem.* IV. 31 (1889); X. 477 (1892).

as $Fe_2Cl_6 . 5\,H_2O$. Further evaporation causes these crystals to effloresce and change to the anhydrous salt in the usual manner.

As we have seen, the maxima of the various curve branches, at *CEG* and *J*, correspond to the melting points of the various hydrates at 37°, 32°·5, 56° and 73°·5 respectively; and at these points melting or solidification of the whole mass can occur at constant temperature. But we have before found this behaviour to be characteristic of the transition points, which in this case are *B*, *D*, *F*, *H*, and *K* (– 55°, 27°·4, 30°, 55° and 66°). This clearly shows two ways in which a constant melting point can be accounted for.

Two liquid components.

When each of the two components can exist as a liquid within the range considered, we shall have the phenomena on the left side of Fig. 16 repeated on the right, where the fusion curve of the second substance will appear.

Thus in Fig. 18 the complete curve is given for mixtures of phenol and water. *A* is the melting point of ice, which is

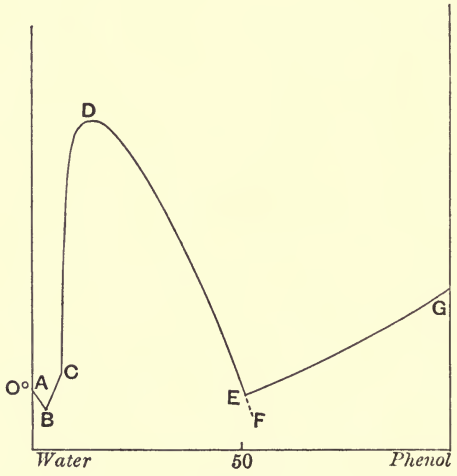


Fig. 18.

gradually lowered to the cryohydric point, *B*, by the successive additions of phenol. *BC* is the solubility curve of solid phenol

in water. At C a new liquid phase appears, consisting of a solution of water in liquid phenol, and at temperatures between C and D, we have two possible liquid phases: (1) phenol in water, the solubility of which is represented by CD, and (2) water in phenol, represented by DE. At D the composition of the two liquid phases becomes identical, and therefore, at temperatures above D, 68°, the liquids are consolute, and only a single liquid phase can exist. G is the melting point of pure phenol, 40°, and GE shows the lowering produced by the addition of water. At E we have a non-variant system, and here there is a constant melting point, phenol being the solvent.

Thus phenol and water are two liquids which above a certain temperature are soluble in each other in all proportions, and below that temperature are not. The consolute temperature varies greatly with different pairs of liquids; with some it is too high to be experimentally reached, but since gases are always miscible with each other, liquids must all become consolute at their critical points if not before. On the other hand the consolute point may be below the freezing point of any of the mixtures. We then have only one liquid phase, and the solubility curves on our diagram disappear, leaving two fusion curves only, which intersect each other at a point. This is illustrated by the case of phenanthrene and naphthalene, the fusion curves of which cut at 48°, forming the non-variant system naphthalene, phenanthrene, solution and vapour.

Alloys.

Precisely similar phenomena are shown by the mixtures of metals known as alloys, which have been extensively studied by many observers including Guthrie, Le Chatelier, Roberts-Austen and Stansfield, Osmund, Stead, Charpy, Roozeboom, and by Heycock and Neville, who use the methods of platinum thermometry[1]. The simplest theoretical case of two consolute substances is realized by the behaviour of silver and copper, for which Heycock and Neville's

[1] Reports, with references, containing accounts of the work on this subject have been given by Roberts-Austen and Stansfield to the Congrès International de Physique, Paris, 1900, I. p. 363, and by F. H. Neville to the British Association, 1900, p. 131.

freezing point curves are shown by Fig. 19[1]. The melting point of silver is 960° and the addition of copper lowers it

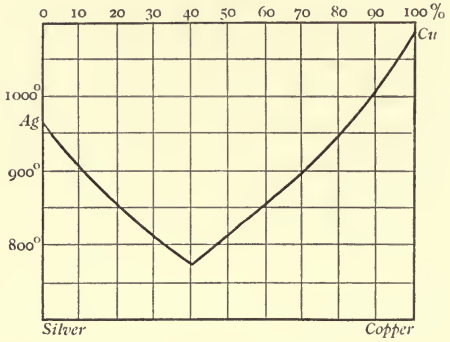


Fig. 19.

regularly and definitely in a monovariant manner till 40 atomic per cents. of copper are present. On the other hand pure copper melts at 1081°·5 and the addition of silver lowers the freezing point till this curve cuts the other at a sharp angle at 777°. Here therefore we have a non-variant system. The four phases which must there exist with a two component system are the two solid metals, the liquid consisting of the melted alloy, and the vapour of the mixed metals, the concentration of the latter being very small. Thus the whole mass can fuse or solidify at 777° without variation of composition and therefore without change of temperature when the atomic percentages are 40 copper and 60 silver. On account of its more uniform texture, as compared with that of other mixtures, this substance is called the Eutectic Alloy.

When the composition of a mixture of two metals, *A* and *B*, is that of the eutectic, the two metals will crystallize simultaneously but in separate crystals. Thus the solid eutectic alloy is a very minute conglomerate, while all other alloys contain large primary crystals of either *A* or *B* embedded in this conglomerate. This has been proved by the microscopic

[1] *Phil. Trans.* A, CLXXXIX. 25 (1897).

work of Osmund[1], Charpy[2] and Heycock and Neville. A drawing illustrating it will be found in a future chapter (Fig. 43).

A liquid whose composition is nearly that of the eutectic shows two changes in the rate of fall of temperature as it is allowed to cool. First a small quantity of one of the pure metals begins to crystallize out, and the rate of cooling is thereby diminished. This process continues till the composition of the liquid phase reaches that of the eutectic alloy, when the whole mass solidifies on further loss of heat without change of temperature, and gives a very definite freezing point. The process of cooling is thus represented by a path which runs vertically downwards till it cuts the freezing point curve, and then travels along it till the eutectic point is reached. In this way two temperatures are obtained, the higher giving a point on the equilibrium curve, the lower showing the eutectic. It will be noticed that this composition of the copper and silver eutectic corresponds to the formula Ag_3Cu_2. Nevertheless the nature of the process as shown by the curve proves nothing more than that a mixture of this composition is in chemical equilibrium with both pure metals at a certain temperature.

The existence of definite compounds, however, is clearly brought out by the investigation of the fusion curve for gold-aluminium alloys, illustrated in Fig. 20[3]. It is quite analogous to the curve for ferric hydrate, and the maxima on the curve near *D* and at *E* and *H*, correspond to the definite compounds Au_5Al_2, Au_2Al and $AuAl_2$, the last named being the purple alloy discovered by Roberts-Austen. The breaks between the lines *AB* and *BC* at *B*, and between *FG* and *GH* at *G*, suggest two other possible compounds, perhaps Au_4Al and AuAl. Thus the curve indicates that the following substances crystallize in succession from the melted alloy; therefore, that it is these substances with which the liquid mixture is saturated in its successive states of equilibrium :—

[1] *Compt. rend.* CXXIV. 1094 and 1234 (1897).
[2] *Compt. rend.* CXXIV. 957.
[3] *Phil. Trans.* A, CXCIV. 201 (1900).

along the branch AB gold pure at A,
„ „ BC (?) Au_4Al nearly pure at B,
„ „ CD (?) Au_5Al_2 or Au_8Al_3 nearly pure at D,
„ „ DEF Au_2Al pure at E,
„ „ FG (?) AuAl maximum not found,
„ „ GHI $AuAl_2$ pure at H,
„ „ IJ Aluminium pure at J.

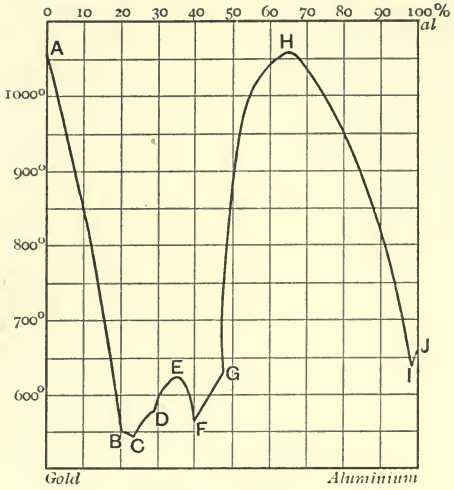


Fig. 20.

Besides these pure compounds, we have systems of constant melting point at C, F and I, which points correspond to eutectic alloys freezing at temperatures of 527°, 569° and 647° respectively.

By the microscopic study of polished sections of these alloys, both by eye and by Röntgen ray photography, Heycock and Neville were able to identify the substances which crystallized out and thus confirm this explanation of the phenomena.

Solid solutions.

In all cases hitherto considered, the addition of one component to a large excess of the other has invariably, at first at any rate, produced a lowering of the melting point. This, as we shall see later, must

always occur when it is the pure component that crystallizes out. When compounds are formed, the initial lowering will be followed by a change in the opposite direction if the compound which solidifies first is richer in the other component than is the liquid. The initial lowering may be confined to a very short length of curve, as in the gold-aluminium diagram in the neighbourhood of pure aluminium (Fig. 20); but when a definite compound is the cause of the main change, the initial lowering is always present. If, however, a solid solution of the two components is possible, that is, if the composition of the solid phase can vary continuously, the addition of one component to the other may at once change the solid which first crystallizes from the solution, and may therefore at once raise the melting point. This phenomenon has been observed in alloys for many pairs of metals. If the two components can mix with each other to form solid solutions of any composition, i.e. are consolute in the solid form as well as in the liquid, no non-variant system is possible, for we cannot assemble the necessary four phases. We shall expect to find for such cases all the types of curves that we shall consider later in detail as representing the boiling points of pairs of consolute liquids. If the composition of the solid solution which crystallizes out is the same as that of the liquid, the whole mass will fuse or solidify without change of temperature, in this respect simulating the behaviour of a definite compound, a cryohydrate, or a eutectic mixture. When the composition of the solid solution which freezes out is not the same as that of the liquid, more complicated cases arise. A general theory of solid solutions has, however, been recently developed by Roozeboom[1] which seems likely to describe all such systems.

In order to explain this theory, we must revert to the consideration of the thermodynamic potential at constant pressure by the graphic method of van Rijn van Alkemade, which we have described in the first chapter. The solid phase can now vary in composition as well as the liquid phase, and there will thus be two continuous curves running across the diagram. The abscissae in the figure represent the composition, the

[1] *Zeit. phys. Chem.* xxx. 385 (1899).

left-hand vertical corresponding to 100 per cent. of the component A and none of the component B, while the right-hand vertical gives 100 per cent. of B and none of A. The ordinates of the first four divisions of Fig. 21 represent the value of the ζ function for unit mass of the solid and liquid phases considered. In the first cases to be examined, the variation of ζ with the concentration is represented for each phase by a simple curve, like that of Fig. 7 on p. 26, with no changes in the direction of curvature.

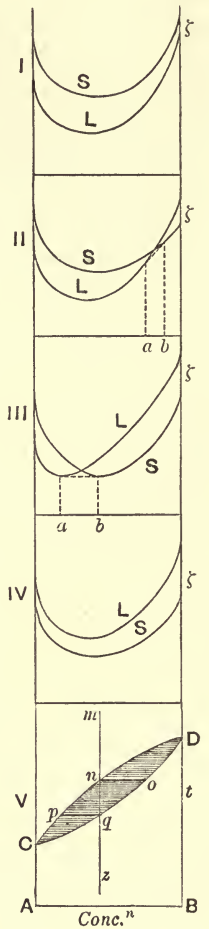


Fig. 21.

The first division of the figure represents the two phases for a temperature above the melting points of both components. The curve for the liquid, which is then the stable phase, must lie below that for the solid. Each end of the curves must, like the left end of the curve in Fig. 7, touch the corresponding vertical axis. At the melting point of either component its solid and liquid will be in equilibrium, and the corresponding ends of the curves will coincide. At some temperature below the melting point of B, for certain compositions, the solid is the stable phase, and the curves will cut each other in the manner shown in the second division of the figure. The third division represents the state of affairs at a still lower temperature, while the fourth division gives the isothermals for a temperature below the melting point of A, when, for the kind of curves illustrated, the liquid phase is never stable, and therefore has everywhere a higher thermodynamic potential than the solid phase. Thus these four diagrams may be taken to be the successive sections of two solid figures, constructed after the fashion of Gibbs'

thermodynamic surfaces, the three axes of which represent concentration, thermodynamic potential and temperature. Over each of these sections the temperature is uniform.

It has already been pointed out (p. 25) that two phases, from one of which a given component can pass into the other, are in equilibrium when the potential of that component in each of them is the same, the potential being defined as the rate of change of the thermodynamic potential of the phase as the component enters it, that is as $d\zeta/dm$, m being the percentage amount of the component B. Now the value of this differential coefficient is given by the tangent to the curve at any point; thus, the two phases will be in equilibrium when their compositions are such that their ζ-m curves have a common tangent. In Division II. then, the phases will be in equilibrium when the liquid has the composition represented by a, and the solid the composition represented by b. At the lower temperature of Division III. similar relations hold.

From these curves the freezing point diagram can now be constructed by imagining a section cut at right angles to the others in such a plane that over it ζ is everywhere uniform. In Division V. of the figure, then, the abscissae, as before, denote the percentage composition of the phases, but the ordinates are now proportional to the temperatures. At the melting point of the pure component A, its solid and liquid are in equilibrium with each other; thus at C, the ordinate on the diagram which corresponds to this temperature, the two phases are represented by a single point. The same thing holds good at D, the melting point of the pure component B. At the temperatures corresponding to Divisions II. and III. of the figure, however, the liquid of composition a is in equilibrium with the solid of composition b, and we thus get two points on our new diagram in the same horizontal temperature line giving the compositions of the liquid and solid which are in equilibrium with each other. Putting in the corresponding points for intermediate temperatures, we finally obtain Division V., in which the upper curve refers to the liquid and the lower curve to the solid phases in equilibrium with each other at the temperatures denoted by the various horizontal straight lines.

These curves are called by Roozeboom the liquidus and solidus, and by Neville the freezing point and melting point curves respectively.

By the help of this freezing point diagram we can trace the changes which occur as a liquid mixture is cooled and solidified into either a mass of mixed crystals or a non-crystalline solid solution. As the temperature falls we pass along a vertical line in the diagram (say *mnqz*) corresponding to the composition of the given mixture. All points above *n* correspond to uniform liquid, and all below *q* to a uniform mass of mixed crystals. While solidification is in progress, the temperature falls from *n* to *q*, the solid forming alters in composition from *o*, in equilibrium with the liquid *n*, to *q*, and the liquid remaining at any instant unfrozen varies from the composition *n*, to the composition *p* which is in equilibrium with the solid *q*. Thus during solidification, the temperature of the whole and the composition of each phase vary continuously.

Other possible forms of the ζ curves are shown in Figs. 22 and 23. In Division I. of Fig. 22, the ζ curves for the solid and liquid are seen first coming into contact, and, in this case, touching each other at a point. The manner in which the curves intersect each other at different temperatures, and the method of deducing the freezing point diagram from them will be obvious from the figure.

In Fig. 22, where the solid curve joins the liquid curve by touching it at a point, the composition of the two phases in equilibrium with each other is identical. This occurs at the highest temperature at which any equilibrium is possible, and the freezing point curve therefore reaches a maximum at this composition. In Fig. 23, where the curves touch each other at a point on separating, similar reasoning shows that the freezing point curve has a minimum at which the composition of the two phases is again the same.

Now when the composition of the solid phase is the same as that of the liquid phase from which it separates and with which it is in equilibrium, the diagram also shows that there is no fall of temperature while solidification is going on nor any change in the composition of the two phases. The whole mass

solidifies at a constant temperature, thus simulating the behaviour of either a pure substance, a compound, or a eutectic mixture.

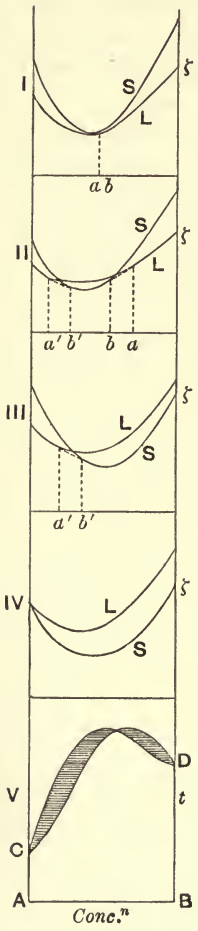


Fig. 22.

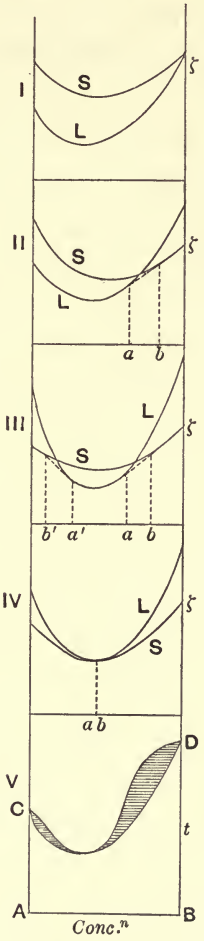


Fig. 23.

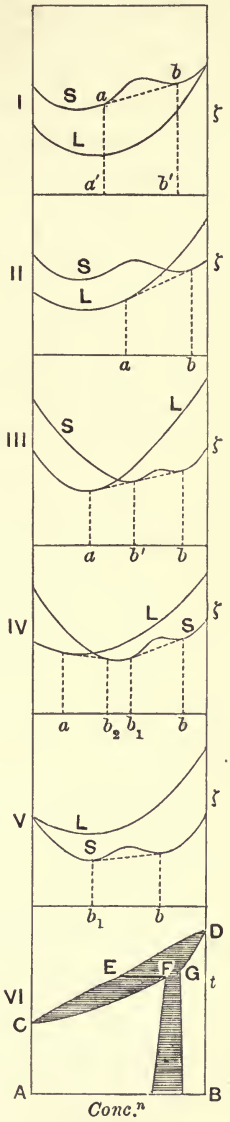


Fig. 24.

There is much danger of confusing these classes of bodies in examining the freezing point curves. A study of the composition of the solid and liquid phases in equilibrium with each other at different temperatures would serve to distinguish between them, and this method has been adopted by van Eyk[1], Reinders[2], and Hissink[3], who have verified Roozeboom's theory for certain mixtures of two salts. In other cases, however, such as those in which the components are metals, there is great difficulty in separating the crystals from the liquid in which they form. The problem must then be attacked in other ways.

If the rate of cooling of the liquid system be observed, the temperature range over which changes from liquid to solid occur will be evident by a decrease in that rate due to the latent heat evolved. Thus the temperatures at which solid begins to form and at which the mass completely solidifies can be determined for different compositions. Both curves of Roozeboom's diagrams can thus be plotted, and the phenomena interpreted. This method has been used by Roberts-Austen and Stansfield[4] and by Heycock and Neville[5]. If mixed crystals are not formed, a second halt in the rate of cooling will, if it exists, be found to coincide with the temperature of the eutectic point, and to appear at the same temperature as the composition is varied. This case has already been described on p. 61.

Another mode of investigation depends on the microscopic study of polished surfaces of the solidified alloys on each side of the summit of the curve. Work on these lines has been done by Charpy[6], Stead[7] and Heycock and Neville.

Another interesting possibility in the form of the concentration-ζ curves is illustrated by Fig. 24. Here the curve for the solid has changes of curvature. Between the points a and b the thermodynamic potential has higher values than it has beyond those points, and thus the compositions between a

[1] *Zeits. phys. Chem.* xxx. 430 (1899).
[2] *Zeits. phys. Chem.* xxxii. 494 (1900).
[3] *Zeits. phys. Chem.* xxxii. 537 (1900).
[4] *Report to the Congrès International de Physique*, Paris, 1900.
[5] Neville, *B. A. Reports*, Bradford, 1900, and Glasgow, 1901.
[6] *Comptes Rendus*, cxxiv. p. 957; *Soc. d'encouragement...*, p. 384, 1897.
[7] *Metallographist*, ii. p. 314.

and b are unstable, the crystals passing spontaneously into mixtures of varying proportions of the solid solutions a and b. The freezing point curve which results will be apparent from the diagrams. At the temperature E, the liquid whose composition is E is in equilibrium with both the solids F and G, and at this temperature a transition from one solid to the other occurs.

Other examples of possible ζ curves, with their corresponding freezing point diagrams, will be found in Roozeboom's paper[1].

The importance of a knowledge of the properties of solid solutions in interpreting a complicated freezing point curve, such as that of the gold-aluminium alloys shown in Fig. 20, will now be apparent. Not only can mixed crystals of pure components exist, but, if compounds are formed, these compounds can form mixed crystals with each other, and the phenomena of solid solutions will also appear between the points on the freezing point curve corresponding to the compounds.

As probable examples of alloys which form mixed crystals, Neville gives the following: copper-tin alloys; alloys of lead-thallium, of bismuth-antimony and of gold-silver; alloys containing zinc or cadmium with either silver, copper or gold.

The theoretical considerations are also well illustrated by some experiments on mixtures of mercuric iodide and silver iodide described by Roozeboom[2]. The freezing point diagram is represented in Fig. 25. Mercuric iodide melts at 257° and silver iodide at 526°. The liquidus curve is the highest in the diagram, and consists of two branches meeting at 242° in a eutectic point. The solidus curves lie below it. While the composition of the system varies from pure HgI_2 to a mixture containing four molecular per cents. of AgI, a solid solution α, of varying composition, is formed, in which HgI_2 may be regarded as solvent. From 18 to 100 per cents. another series of solutions β, in which AgI is solvent, exist. Solid solutions of composition between 4 and 18 per cents. of AgI cannot be obtained, and in this part of the field we have a varying

[1] *Zeits. phys. Chem.* xxx. 385 (1899).

[2] *Kon. Akad. Wetensch. Amsterdam*, June 30, 1900.

conglomerate of the limiting examples of α and β. The upper boundary of these areas gives the solidus curve, which realizes the theoretical solidus of Fig. 24.

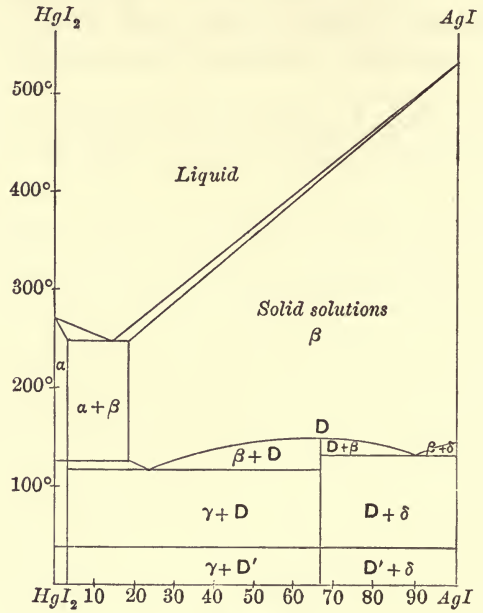


Fig. 25.

If mixed crystals with 4 per cent. of AgI are cooled, they undergo a change near 127°, owing to the transition of the HgI_2 from the rhombic to the tetragonal form. If, on the other hand, a mixture of the composition $HgI_2 2AgI$ is cooled, at 157° the pink mixed crystals suddenly change into a red chemical compound having the same composition, represented by *D* on the diagram. This is exactly comparable with the solidification of a compound from a liquid solution, and, as in the compounds of ferric chloride and water of Fig. 17, or those of gold and aluminium of Fig. 20, the curve sinks on each side of this point, and forms eutectic mixtures of $HgI_2 2AgI$ with HgI_2 at 118° and with AgI at 135°. Below these temperatures then all solid mixtures are transformed into conglomerates of double salt either with HgI_2 or with AgI. When these conglomerates

are cooled to 45° the compound changes from red to yellow whether it is pure or mixed with one of the components.

Similar phenomena have been traced in the case of alloys of copper and tin by Heycock and Neville[1]. Here also definite changes in crystalline structure take place on cooling at definite temperatures, long after solidification has occurred. The experiments consisted in measuring the freezing points of varying mixtures, and suddenly fixing the structure of the solid alloy at any temperature by plunging it into cold water. The surface was then polished, etched with acid, and examined under a microscope. The different crystalline species could thus be recognized by their characteristic forms.

Two volatile components.

Since leaving the original qualitative diagrams we have studied in detail only the relations between concentration and melting point. Similar phenomena are found when boiling points are examined. Roozeboom's theory of solid solutions may be applied to consolute liquids, the possible variations of ζ with concentration being plotted for the liquid and vapour phases. Boiling point curves will then be obtained similar to the freezing point curves of Figs. 21 to 24. Experimental results usually trace only the liquidus curve, analogous to the solidus curves given above; few investigations of the composition of phases containing mixed vapours have been made.

Another useful modification of method consists in measuring the vapour pressures of two components at varying concentrations. If the number of phases present is that giving a monovariant system, the changes might be represented by a projection of the monovariant p-t-c curve on the p-c plane. If the system is divariant, it is represented by a surface in the solid model, and we can draw a section of this surface in that same plane corresponding to any given constant temperature. While the projection curves serve to illustrate the varying vapour pressures of saturated solutions of solids at different temperatures, and therefore concentrations, the vapour pressures of mixtures of volatile liquids are often measured in divariant

[1] *Proc. R. S.* LXIX. 320; 1902.

systems, and are thus better set forth by section diagrams in the concentration-pressure plane.

Pairs of liquids, as we have seen, must be divided into three classes—(i) those which will not mix at all, (ii) those partially soluble in each other, (iii) those soluble in each other in all proportions. The laws of vapour pressure are different for each case.

(i) With immiscible liquids the vapour pressure is equal to the sum of those of the constituents. This can be proved by passing the vapour of one boiling liquid into the other and examining the vapour which comes through; in it the two substances will be present in the ratio of their own vapour pressures. The sum of the two pressures will, at the boiling point of the mixture, be equal to the atmospheric pressure, so the boiling point must be lower than that of either constituent. But this is usually masked; for if one liquid forms a layer over the other, the mixture bumps violently if the more volatile liquid be below, while, if the positions are reversed, it is only the upper liquid which evaporates.

(ii) The behaviour of partially miscible liquids has been studied by Konowaloff[1], who found by experiment that the solution of a liquid A saturated with a liquid B exerts at a

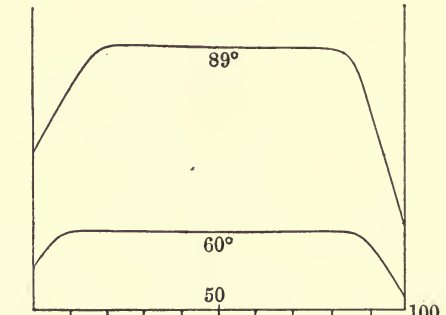


Fig. 26. Percentage of alcohol.

certain temperature the same vapour pressure as that which a solution of B saturated with A exerts at the same tempera-

[1] *Wied. Ann.* XIV. 219 (1881); account with figures in Ostwald's *Lehrbuch.*

ture. Konowaloff measured the vapour pressures of mixtures of two liquids of varying composition and at different temperatures. One result of his observations is shown by the form of the curve in Fig. 26, which gives the relation between percentage composition and vapour pressure of a mixture of water and isobutyl alcohol at 89° and at 60°. While the percentage of alcohol is less than that required to saturate the water, the system is divariant and the vapour pressure increases with the percentage of alcohol. When the solution is saturated, the system becomes monovariant and the vapour pressure is independent of the excess of alcohol present. Such a mixture has then a constant boiling point, and the composition of the vapour is always the same. This constant vapour pressure is found to be smaller than the sum of those of the two constituents. When the percentage of alcohol is so large that all the water present can dissolve in it, the vapour pressure again alters with the composition of the solution, and finally sinks to its value for the pure alcohol. If a mixture represented by any point on either of the inclined portions of the curve be distilled, the composition of the vapour and the boiling point will gradually alter till the liquid present in large excess is finally left nearly pure. The curve of Fig. 26 is not directly derived from a complete *p-t-c* model, for it represents two variable liquid phases: the abscissae give the composition of the whole system, not of one phase only.

(iii) Mixtures of liquids which are soluble in each other in all proportions give a single liquid phase. The vapour pressure curves can therefore be derived from the model by cutting sections of the corresponding divariant surfaces in the *p-c* plane. The following curves give Konowaloff's results. They at once show how the mixtures will behave on distillation. The tendency is (since there is no constancy in the composition of the vapour) for that particular mixture which has the greatest vapour pressure, and therefore the lowest boiling point, to come off first in greatest quantity, and in this way by repeatedly redistilling we at last get a distillate which has the composition corresponding to this lowest boiling point. Thus with water and propyl alcohol,

which mixture has a maximum vapour pressure when the percentage of alcohol is about 75, the final distillate obtained will have that composition.

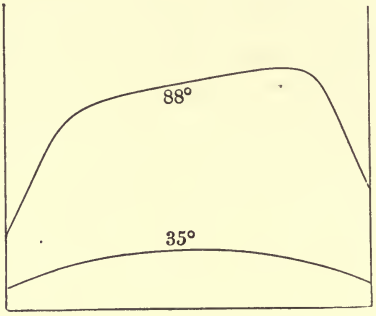


Fig. 27. Water and propyl alcohol.

The curves for water with ethyl alcohol and with methyl alcohol show that in these cases no maxima are reached, so that by repeated distillation we get a nearly pure alcohol in the receiver, and pure water is left in the retort after the first boiling. It is much easier to get water free from alcohol than alcohol free from water, because the influence of a little alcohol

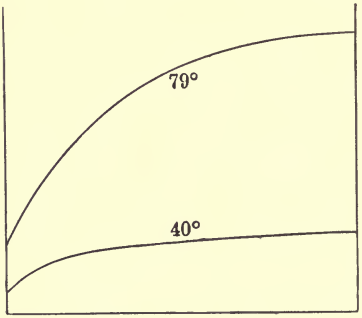


Fig. 28. Water and ethyl alcohol.

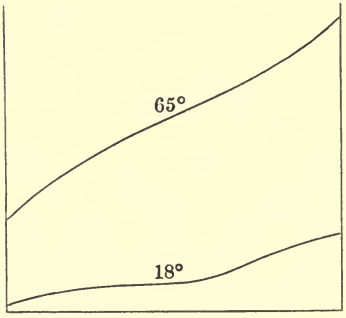


Fig. 29. Water and methyl alcohol.

on the boiling point of water is so much greater than that of a little water on the boiling point of alcohol. This case is of great importance in practice, for by such means mixed liquids of different boiling points are separated in the chemical

laboratory by the process of "fractionation." We now see that this can only give perfect separation when the type of the vapour pressure curve is that shown in Figs. 28 and 29.

A mixture of water and formic acid shows greater influence of the constituents on each other. The vapour pressure of the mixture is lower than that of either constituent, and reaches a minimum at a percentage of acid of about 73. All other proportions will therefore tend to distil over sooner than this, and finally we shall get a residue left in the retort containing 73 per cent. of acid. This will then distil over unchanged.

The last case really includes such liquids as aqueous solutions of nitric or hydrochloric acid, which were once thought

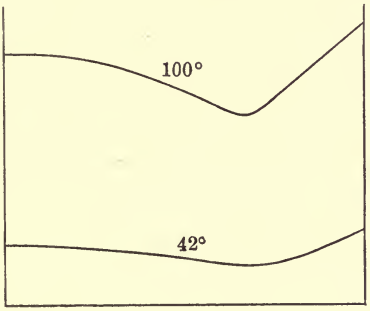


Fig. 30. Water and formic acid.

to show definite chemical combination in the proportions of the mixture which finally distilled over unchanged. Roscoe[1] however proved that the composition of this distillate varied with change of pressure, and the facts are fully explained by the vapour pressure curves given above.

Since the boiling point is higher as the vapour pressure is lower and vice versa, Figs. 26 to 30, if inverted, will qualitatively represent the experimental relations between concentration and boiling point. Their connexion with the theoretical solidus curves of Figs. 21 to 24, as well as the analogy between the boiling points of the partially consolute liquids of Fig. 26

[1] *Quart. Journ. Chem.* XII. p. 128 (1859), or *Treatise on Chemistry*, vol. I. p. 138.

and the melting points of the partially consolute solids of Fig. 25, will then be apparent.

Three components.

When three components are present the equilibria become much more complicated. The Phase Rule shows that for three components it is necessary to assemble five phases for a non-variant system, four for a monovariant and three for a divariant. Plane pressure-temperature diagrams can be constructed, the concentration being assumed constant, but some modification is necessary when we require to plot concentration and temperature or concentration and pressure. We can take a solid figure so as to get three axes, the temperature in one case or the pressure in the other being measured vertically, and then project this figure on to its base. The base may conveniently be in the form of a triangle, the total mass of the components being kept constant. The corners of the triangle are taken to represent the three pure components and the composition of any mixture in atomic percentages is represented by its position in the triangle, the position being the centre of mass of the three components placed at the corners. Thus Guthrie[1] has investigated mixtures of potassium, sodium and lead nitrates, and his results are shown in Fig. 31. At A we

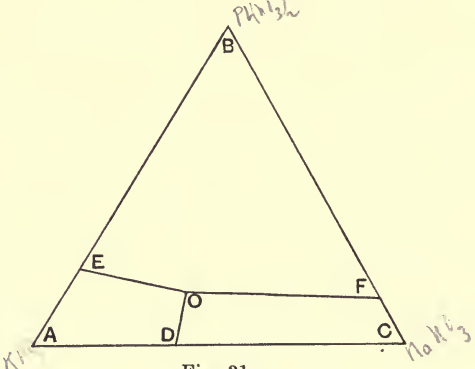


Fig. 31.

have pure potassium nitrate melting at 340°. Lead nitrate would exist pure at B, but since it decomposes before fusing,

[1] *Phil. Mag.* (5), XVII. 472 (1884).

the temperature is unknown. At the other corner C we have sodium nitrate which melts at 305°. The point D represents the composition of the eutectic mixture of the potassium and sodium salts; its fusion point is 215°. In like manner E (207°) and F (268°) correspond to the eutectics of the other pairs of substances. At O (186°) is found the non-variant system consisting of the three solid salts, the mixed liquid and the vapour.

A fuller consideration of three component systems, together with many more examples of the phenomena of systems of one and two components will be found in Bancroft's book on "The Phase Rule[1]."

The problems of solution.

In this chapter we have studied the general phenomena of solutions, considered as mixtures of two components, of which the equilibria are completely determined qualitatively by thermodynamic principles and the phase rule. This treatment has already enabled us to survey our subject, and to examine its main outlines and its bearing on the general problem of the equilibrium of phases. The diffusion of dissolved substances and the electrical properties of solutions, since we are then studying phenomena which are not those of equilibrium, will involve other methods, but until we reach this part of our subject, we shall be chiefly concerned with the more thorough investigation of the relations we have already traced by aid of the phase rule. The detailed study of solubility will be but the quantitative examination for certain cases of the solubility curves shown in the diagrams of this chapter; while the experiments which have been made on the freezing points of solutions, dilute or concentrated, and on the vapour pressures, are merely more accurate delineations of their corresponding curves. Thus the phase rule is of importance, not only in placing the theory of equilibrium of phases on a sound basis, but also as furnishing a means of classification for the phenomena of solution, which enables us to arrange our material in logical and scientific sequence, and gives a standpoint whence we can trace the relations of the whole subject.

[1] Ithaca, New York, 1897.

CHAPTER IV.

SOLUBILITY.

General problem of solubility. Supersaturation. Solubility of gases in solids. Solubility of gases in liquids. Henry's law. Solubility of gases in salt solutions. Solubility of liquids in liquids. Solubility of solids in liquids. Influence of pressure on the solubility of solids. Solubility of mixtures. Solubility in mixed liquids. Tables of solubility.

General problem of solubility.

THE solubility of a substance, which can be defined as the quantity of solute required to saturate a given mass of solvent, depends, as we have seen, on the change produced by the act of solution in the thermodynamic potential of the system, equilibrium being always reached when that potential is a minimum. Very little is yet known about the physical and chemical conditions which determine the solubility of a substance in a given solvent, in fact the essential nature of the process of solution must be regarded as at present uncertain. It has been noticed that solution is more likely to occur if the solute and solvent are somewhat alike chemically, but, even to this extent, no general rule can be framed. Still it is found that mineral salts and acids are in general readily dissolved by water, while benzene, for example, is a more likely solvent for organic substances.

The phase rule and the principles of thermodynamics have enabled us to trace the course of the qualitative phenomena of the equilibrium of the phases of two components, including the problem of solubility as a special case. We have now to examine in greater detail the quantitative relations, and to

give some further account of the experimental determinations which have been made on the subject.

In a saturated solution there is equilibrium between the solid and the solution, and any structural change in either of the two will produce a change in the equilibrium. Thus, as we explained on p. 53, the change in the nature of the solid crystals of hydrated sodium sulphate, $Na_2SO_4 . 10\,H_2O$, which are transformed into the anhydrous salt Na_2SO_4 at a temperature of 32°·6, causes a sudden change of direction in the solubility curve (Fig. 32). The transition point is the temperature at which the non-variant system salt-hydrate-solution-vapour can exist in equilibrium; below this temperature the solubility of sodium sulphate increases with rising temperature, above it the solubility diminishes. This change was formerly explained by the supposition that below 32°·6 hydrated salt is present in solution,

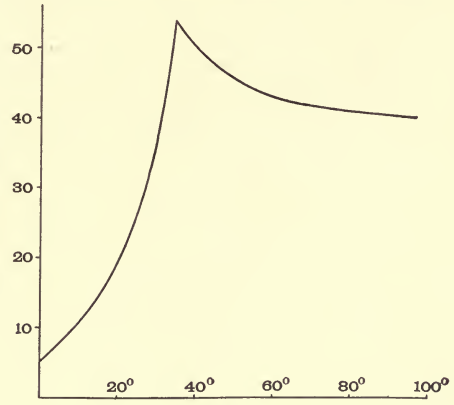


Fig. 32.

and above that temperature the liquid contains the anhydrous substance. Our present knowledge of the general problem of equilibrium shows at once that such a supposition is unnecessary; moreover, there is evidence of a direct nature which proves it to be untenable. If this view were correct, we should expect the physical properties of the solution to differ from each other above and below the transition point, but in none of those properties has a sudden change been found[1].

[1] Ostwald's *Lehrbuch*, or *Solutions*, p. 74.

Supersaturation.

A similar continuity of properties holds good at the point of saturation. None of the curves indicating the variation with concentration of any physical property of the solution exhibit a sudden change of curvature as the saturation point is passed and a supersaturated solution obtained. This has been shown for the freezing points by Coppet[1], for the electrical conductivities by Beetz[2], Kohlrausch[3] and Heim[4], and for the densities, specific heats and heats of solution by Bindel[5].

It will thus be evident that there is nothing abnormal in the condition of a supersaturated solution; there is merely no solid present to induce equilibrium, and the case corresponds exactly to that of an under-cooled liquid. The facility with which a solid is spontaneously deposited by a liquid determines the conditions under which a supersaturated solution of the given substance can be produced. It is found that such solutions can with care be almost always obtained; but it has been noticed that their production is usually easier in the case of salts which freely form large crystals, particularly when those crystals are hydrated. The phenomena of the supersaturation of air with water vapour, to which we have referred on p. 43, are closely analogous to those now under consideration. Just as a proper nucleus will at once induce precipitation of water from supersaturated air, so crystallization is started in a supersaturated solution by the presence of a fragment of a crystal, either of the substance with regard to which the solution is supersaturated or of any body isomorphous with it.

In the case of supersaturated water vapour, we have seen that it is the existence of free energy due to surface tension, which is proportional to the area of contact between water and air, that makes it so difficult for very small drops of water to be formed spontaneously, and requires the presence of nuclei to

[1] *Ann. Chim. Phys.* (4) XXIII. 366 (1871).
[2] *Pogg. Ann.* CXVII. 1 (1862).
[3] *Wied. Ann.* VI. 28 (1879).
[4] *Wied. Ann.* XXVII. 643 (1886).
[5] *Wied. Ann.* XL. 370 (1890).

induce precipitation. While, as seen on p. 45, the mechanism of the process is probably different, it is still likely that in the crystallization of solutions, the free energy of surface tension plays an important part, and it is probable that it is most difficult to start precipitation in those solutions where the energy of the surface between the liquid and the possible solid is greatest.

The same free energy of surface tension causes the large drops of water in a collection of various sizes to grow at the expense of the smaller ones which have a larger area for a given volume, for the total free energy tends to a minimum; and something of the same kind seems to occur in the case of solutions, the smaller crystals deposited from a saturated liquid having been seen to disappear while the larger ones have increased in size[1]. Gibbs has pointed out[2] that, in large crystals, the surface energy will not have the same value on the different faces, which will consequently be in equilibrium with solutions of different concentrations. Thus, in a saturated solution, certain faces will grow and certain other faces dissolve, and the crystal will eventually be bounded solely by the latter. In very minute crystals, the surface energy of a side will be affected by the other sides, and it seems likely that the form is then determined by the simple relation that the total surface energy must be a minimum for the volume of the crystal. In this case, the crystal will tend to possess a definite shape as well as definite angles. The small disturbing effect of gravity will make a crystal grow more readily in the upper or lower parts of the liquid, according as its growth causes expansion or contraction.

Solubility of gases in solids.

Gases form dense films over the surfaces of glass vessels, and probably of all other solids. In certain cases, such as the action of platinum and palladium on oxygen and hydrogen, the gas absorbed seems to penetrate the mass of the solid, though, if these solids be considered as porous, this again may be only a surface action. It is still

[1] For this interesting observation the author is indebted to Lord Berkeley.

[2] *Trans. Connect. Acad.* III. 494 (1878).

uncertain whether the bodies thus formed are more of the nature of chemical compounds or of solid solutions.

The film of air, etc., which covers the surfaces of glass vessels, is exceedingly difficult to remove. This is shown by the variations of pressure inside exhausted bulbs, particularly when electric discharges are passed. Even heating such a bulb to a high temperature seems to fail in completely removing the gas. The influence of the area and nature of the walls of the containing vessel, which is so marked in the reactions between gases[1], may be largely or entirely due to the effect of the condensed film. For example, dry ammonia and hydrochloric acid gases will not combine, though, if moisture be present, a cloud of ammonium chloride is at once formed. A perfectly dry mixture of oxygen and hydrogen will neither explode when heated nor combine gently at temperatures of 400° or 500° Centigrade as will the moist gas. There seems reason to believe that this action of moisture depends on the film of water or other concentrated substance formed on the surface of the vessel, or on the minute particles of water scattered throughout the volume. It is possible that chemical action can only occur between the gases when they are dissolved in this water, a possibility which might reduce all chemical actions to those taking place in solution[2].

The absorption of oxygen, hydrogen and other gases by such metals as platinum and palladium was discovered by Graham[3], who gave the process its name of occlusion, and has since been studied by Deville and Troost[4], Dewar[5], Troost and Hautefeuille[6], Berthelot[7], Favre[8], Roozeboom and Hoitsema[9] and by Mond, Ramsay and Shields[10].

[1] See, for instance, Van 't Hoff, *Studies in Chemical Dynamics* (1896), p. 43.

[2] See J. J. Thomson, *Phil. Mag.* xxxvi. 313 (1893), and C. T. R. Wilson, *Phil. Trans.* A. cxcii. 452 (1899).

[3] *Proc. R. S.* xv. 223 (1867), xvi. 422 (1868), xvii. 212 and 500 (1869).

[4] *Comptes Rendus*, lvii. 894.

[5] *Phil. Mag.* [4] xlvii. 324 and 342 (1874); *Proc. Chem. Soc.* clxxxiii. 192 (1897).

[6] *Compt. Rend.* lxxviii. 686; *Chem. Soc. Journ.* xxvii. 660 (1874).

[7] *Ann. de Chim. et Phys.* [5] xxx. 519 (1883).

[8] *Compt. Rend.* lxxvii. 649, and lxxviii. 1257 (1874).

[9] *Zeits. phys. Chem.* xvii. 1 (1895).

[10] *Phil. Trans.* A. clxxxvi. 657, cxc. 129, cxci. 105 (1893–7 and 8).

Both platinum and palladium can be prepared by chemical or electrolytic precipitation as very porous black deposits, and, in this state, they show the property of occlusion in the highest degree. A certain quantity of oxygen is occluded from the atmosphere, and any hydrogen admitted will first combine with this oxygen to form water. This fact was overlooked by the earlier observers of the absorption of hydrogen, and has vitiated their conclusions. Mond, Ramsay and Shields found that when platinum black is heated in an atmosphere of oxygen at ordinary pressure, absorption goes on till the temperature is raised to about 360°, when the gas is expelled; the heat evolved by the occlusion being about 1100 calories, or 11 K., where K. denotes 100 calories, for each gram of oxygen absorbed, which gives 176 K. per atomic weight in grams. The same observers investigated the absorption of hydrogen by allowing it to enter the metal at the ordinary temperature and form water, which is pumped out at 184° together with the excess of gas, the latter being readmitted in an ice calorimeter. The heat of occlusion was found to be 68·8 K. per gram of hydrogen, and to be the same for the hydrogen which can be pumped out of the platinum at ordinary temperatures as for that which only comes off at 184°. The heat of occlusion of oxygen is nearly the same as the heat of oxidation, thus suggesting that the process is a superficial oxidation. In the case of palladium, it is probable that the oxide PdO is formed; on the other hand the only evidence for the existence of compounds with hydrogen is the approximate correspondence of the completely saturated palladium with the formula Pd_3H_2, while Hoitsema concludes, from a study of the vapour pressures of palladium containing hydrogen, that two immiscible solid solutions are probably formed. Palladium absorbs about 850 times its volume of hydrogen, the thermal evolution, which is about 46·4 K. per gram of hydrogen, remaining constant throughout the process. It is likely that the increase of absorbing power with a rise in temperature noticed in certain cases, is due to a corresponding increase in the rate of diffusion of the occluded gas from the saturated outside layers to the inner parts of the metal. The same difficulty of diffusion is probably the reason of the much less marked absorbing power

of the metals in the form of dense foil, when the area exposed to the direct action of the gas is very much less than it is when they exist in the spongy black condition.

Solubility of gases in liquids.

There appear to be two different classes of solutions of gases in liquids. Sometimes, as in the case of hydrochloric acid dissolved in water, the gas cannot be completely expelled either by lowering the pressure or increasing the temperature. On the other hand, air, oxygen, hydrogen and certain other gases can be thus removed, although the separation of the last traces of gas is a process of extreme difficulty. Nevertheless, in these cases, the solvent exerts a selective action, the gases differing from each other in solubility.

It is found that, in general, the solution of a gas in water, even when the liquid is nearly saturated, is accompanied by an evolution of heat. From this it follows by the principles of thermodynamics that the solubility will decrease with rising temperature.

In an experimental determination of solubility it is necessary to take precautions to ensure complete saturation, for the process of diffusion of matter from one portion of a liquid to another is very slow. Many forms of apparatus have been devised, the simplest being that used by Bunsen, who placed a measured volume of the gas in a graduated tube over mercury and added a certain volume of the liquid. The tube was then shaken in a water bath of constant temperature, the open end being screwed against an india-rubber plate. By repeatedly opening the end under mercury and then closing it again and shaking, saturation was obtained, the solubility being determined by measuring the volume of gas left over, the volume of the liquid, and the final pressure.

Ostwald[1] has found an absorptiometer, constructed after a design due to Heidenhain and Meyer, to be both convenient and accurate. It is represented in Fig. 33. The vessel *C* is filled with the air-free liquid, and, running out a measured volume by raising the tube *B*, an equal volume of gas can be

[1] See *Lehrbuch*, or *Solutions*.

introduced through a flexible lead tube from the graduated vessel A. The tubes A and C are immersed in a water bath, and C is constantly shaken to cause absorption.

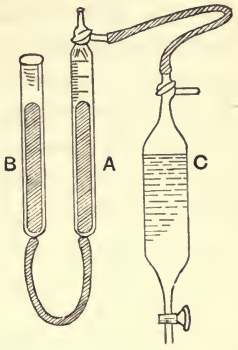


Fig. 33.

The solubility of a gas has been defined by Ostwald to be the ratio of the volume of gas absorbed to the volume of the absorbing liquid, at any specified temperature and pressure, say S is equal to v/V. Bunsen used a more complicated constant, which he called the absorption coefficient. It is obtained from Ostwald's solubility by reducing the volume of gas absorbed to 0° C. at the pressure of the experiment. In certain cases we shall see that the volume of gas absorbed is independent of the pressure, so that if β is Bunsen's absorption coefficient, and α the coefficient of gaseous expansion,

$$S = \beta(1 + \alpha t).$$

Bunsen and others[1] have determined many absorption coefficients for water and alcohol. The following are some of their results taken from Ostwald's *Lehrbuch*.

	Hydrogen		Oxygen		Carbon Dioxide	
Temp.	In Water	In Alcohol	In Water	In Alcohol	In Water	In Alcohol
0°	0·0215	0·0693	0·0489	0·2337	1·797	4·330
15°	0·0190	0·0673	0·0342	0·2232	1·002	3·199

Henry's Law.

Henry proved that the mass of a gas such as oxygen dissolved in water is proportional to the pressure, and established this law as an approximation by a series of experiments on five gases at pressures varying from one to three atmospheres[2]. Since the volume of a given mass of gas varies inversely as its pressure, it follows that the

[1] Bunsen, *Pogg. Ann.* XCIII. p. 10, 1855; Winkler, *Berichte*, XXII. p. 1439, 1899; Timofejeff, *Zeitschr. f. physikal. Chem.* VI. p. 141, 1890.

[2] *Phil. Trans.* 1803.

volume which is dissolved, measured under the pressure it exerts above the liquid, is independent of that pressure.

The reason of this result is suggested by the dynamical view of equilibrium, which imagines that saturation is reached when the quantity of gas going into solution per second is equal to the amount coming out. If the pressure is reduced, the number of gaseous molecules striking the liquid, and therefore the number per second retained by it, are reduced in the same proportion, while the rate at which they leave is at first unchanged. The concentration of the gas in solution is thus gradually lowered till equilibrium is again attained, and the concentration bears once more its old relation to the external pressure. At first sight it would appear that the solubility of a gas should be unaffected by an alteration of temperature, since the number of molecules impinging on the surface from within and without would vary in the same proportion. But here the influence of the solvent comes in, and the interaction between it and the gas is changed by increase of temperature so that the solubility becomes less.

Bunsen confirmed Henry's law in a series of more accurate experiments, both by varying the pressure in his absorptiometer and by using a mixture of gases. If we have a volume of gas at atmospheric pressure, consisting of equal parts of two constituents, the total pressure is obviously due half to one and half to the other, so that, restricting our consideration to one gas, the pressure it exerts is half that of the atmosphere. In this way by using mixtures in which the proportion of one gas continually diminished, its pressure could be reduced from one atmosphere to zero, and it was found that the mass absorbed varied in the same proportion.

In the case of many very soluble gases the phenomena are not so simple. For ammonia at 100° C. the law of Henry holds good[1]; but if observations be made at lower temperatures, the mass of ammonia absorbed is not proportional to the pressure, and the curve drawn to show the variation of solubility with pressure when the temperature is kept at 0° C. shows two changes of curvature. Sulphur dioxide behaves like ammonia,

[1] Sims, *Annalen*, CXVIII. p. 345, 1861.

the law only holding true above 40°. Hydrogen chloride cannot be entirely removed from solution in water either by reducing the pressure or by boiling. If aqueous hydrochloric acid be distilled, its strength will either increase or diminish till a liquid of a certain composition remains, which distils over unchanged. This composition depends on the pressure at which the operation is carried on; at normal atmospheric pressure the proportion of hydrogen chloride is 20·24 per cent., at 50 mm. of mercury pressure the proportion is 23·2 per cent., and at 1800 mm. it sinks to 18 per cent. As we have seen, the solution left is that mixture which possesses the highest boiling point under the condition of the experiment.

Solubility of gases in salt solutions.

The coefficient of absorption for a gas appears to be lowered when a salt which does not act chemically on the gas is previously dissolved in the water. In general, however, chemical action does occur, and the gas dissolved may be considered to consist of two parts—one being held chemically by the salt nearly independently of the pressure, and the other varying with the pressure in accordance with Henry's law. Good examples of this are seen when carbon dioxide is dissolved in a solution of sodium carbonate or disodium phosphate. Solutions of similar salts of equivalent strength absorb nearly equal quantities of carbon dioxide—e.g. the sulphates of zinc and magnesium[1].

The effect of mixing another liquid with the water is similar to that of dissolving a salt in it—the absorption coefficient for a gas is reduced. This holds even with such substances as sulphuric acid and alcohol, which are themselves in the pure state as good as or better than pure water in absorbing power. Thus with sulphuric acid Setschenoff found for carbon dioxide a minimum absorption coefficient when the composition of the liquid was $H_2SO_4 . H_2O$. His results are as follows:—

H_2SO_4	$H_2SO_4 + \frac{1}{2}H_2O$	$H_2SO_4 + H_2O$	$H_2SO_4 + 2H_2O$	$H_2SO_4 + 58H_2O$	H_2O
·923	·719	·666	·705	·857	·932

[1] Setschenoff, *Mém. de l'Akad. Pétersb.* XXII. No. 6, 1875; *Z. f. physikal. Chemie*, IV. p. 117, 1889.

These numbers show that a mixture of sulphuric acid and water absorbs less carbon dioxide than either liquid does when pure. Similar relations are found to hold good for other physical properties, such as the electrical resistance and the viscosity.

Solubility of liquids in liquids.

Solutions of liquids in liquids have been considered on pp. 58 and 71 under the head of two liquid components, from the point of view of the phase rule. As we then saw, there are three classes into which pairs of liquids can be divided. Those in the first class are mutually soluble in all proportions; thus mixtures of alcohol and water, or of water and sulphuric acid, can be prepared of any composition. Those in the second class are soluble in each other but not in all proportions; thus water will dissolve about ten per cent. of ether, and ether about three per cent. of water, but if either substance be present in excess it separates out, forming a definite layer. The third class, which is small, consists of liquids which are insoluble in each other. The divisions between these classes are dependent on external conditions, for liquids which are only partially miscible at ordinary temperatures may mix in all proportions when heated, and it is probable that all liquids approach the condition of complete miscibility as they approach their critical points[1].

Measurements of the mutual solubility of liquids have been made by Alexejeff[2], who placed weighed quantities in a sealed tube and noted the temperature at which the mixture became homogeneous.

The form of the solubility curve for a pair of partially miscible liquids is shown in Fig. 34, in which the abscissae represent temperatures and the ordinates percentages of dissolved substances in 100 parts of the solution. The curve *a* represents a solution of water and phenol; the curve *b* water and aniline phenolate. At low temperatures there are two

[1] It is stated (Watts' *Dict.* Art. Solutions 1.) that diethylamine and water, though miscible in all proportions at low temperatures, cease to be so when heated.

[2] *Wied. Ann.* XXVIII. p. 305, 1886; *Chem. Centralblatt*, pp. 328, 677, 763, 1882.

definite states in which equilibrium is attained—the lower branch of the curve representing a solution of phenol in water, the upper branch a solution of water in phenol.

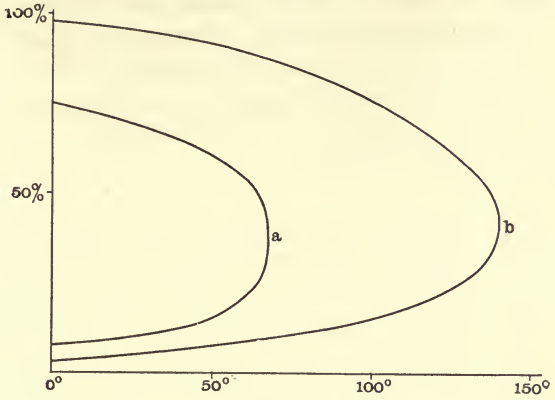


Fig. 34.

Solubility of solids in liquids.

It is fairly easy to make an approximate determination of the amount of a solid required to saturate a given quantity of a liquid, but when accurate results are needed, the problem becomes one of extreme difficulty. There are two methods of procedure. The first is to keep the liquid in contact with an excess of the solid for many hours at as constant a temperature as possible, by immersing the vessel containing the mixture in a water bath with an automatic thermal regulator, while the apparatus is either constantly or intermittently shaken. The second method consists in heating the liquid with excess of solid to a temperature above that at which the determination is to be made, and then allowing it to slowly cool in contact with the solid till the temperature in question is reached.

Whichever process is adopted, a quantity of the solution is then analysed either chemically or by evaporation, and the amount of solid in it determined. There is often a considerable difference in measurements made in these two ways, the second yielding higher results than the first. The attainment of the state of equilibrium seems to be a very slow process, even when the mixture is kept constantly stirred.

The Earl of Berkeley, who has made many laborious experiments on this point, finds that the time needed before the saturation is approximately complete varies with the nature of the salt, the mass of solid present, and the temperature. Even with constant and rapid stirring, in certain cases as much as forty-eight hours may be required.

The solubility is usually expressed as the parts by weight of the solid which dissolve in one hundred parts of the solvent to form a saturated solution.

Influence of pressure on the solubility of solids.

The solubility of solids, owing to the small changes in volume produced by solution, is only slightly affected by pressure, and accurate experimental determinations are very difficult. The principles of thermodynamics indicate that the chief conditions determining the change of solubility with increasing pressure are the heat of solution of the salt in the nearly saturated solution, and the change in volume on solidification. The few experiments which have been made seem to confirm this conclusion. Van 't Hoff states[1] that ammonium chloride, which expands on solution, loses solubility by 1 per cent. for 160 atmospheres, while copper sulphate, which contracts, gains by 3·2 per cent. for 60 atmospheres.

Influence of temperature.

The influence of temperature on the solubility of solids in liquids has been constantly studied from the time of Gay Lussac to the present day. As a general rule solubility increases with temperature, though several exceptions to this rule are known, for example, calcium hydroxide, and sodium sulphate between the temperatures of 33° and 100°. It is impossible, when studying the influence of temperature on solubility, to overlook the analogy between the solution of a solid in a liquid and the evaporation of a liquid into a closed vacuous space. Just as for every temperature there is a definite quantity of vapour present in the space when equilibrium is reached, so there is a definite quantity of solid dissolved. Increase of temperature causes in

[1] *Lectures on Theoretical and Physical Chemistry*, p. 34.

the one case more liquid to evaporate, and in the other more solid to dissolve, till a new state of equilibrium is reached. We shall see hereafter that, while a liquid exerts a vapour pressure, a solid in solution exerts a pressure which can be recognized and measured by means of certain phenomena, to which the name of osmose has been given. The analogy between the two processes seems thus very close, and is borne out by the general similarity of the solubility curves (Fig. 35) to curves which show the variation of vapour pressure with temperature.

As the vapour pressure curves end at the critical points of the liquids, so the solubility curves end at the melting points of the solids. The phenomena beyond depend on the miscibility or non-miscibility of the liquid solvent and the fused solid, and are qualitatively described by the principles of the phase rule.

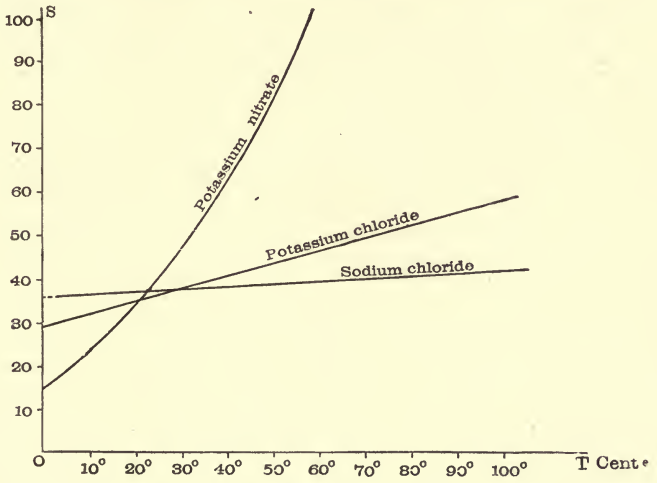


Fig. 35.

A long series of investigations on the influence of temperature on solubility has been made by Etard and Engel[1], who examined various solutions at temperatures above 100°, by heating them in sealed tubes. They find that solutions of many sulphates

[1] *Comp. Rend.* 1884–8, XCVIII. pp. 993, 1276, 1432; CIV. p. 1614; CVI. pp. 206, 740.

have solubility curves showing maxima at definite temperatures, while certain calcium salts have curves giving minimum values.

If solubility be defined as the parts of salt in 100 parts of solution, instead of 100 parts of solvent, each part of the curve according to these observers generally comes out as a straight line. Thus the curve for copper sulphate consists of three straight lines which join each other consecutively at 55° and 105°.

As we have already remarked, the solubility increases or diminishes with rising temperature, the action depending on the absorption or evolution of heat when some of the solute dissolves in the nearly saturated solution, so that the thermal effect must change sign where maxima or minima occur in the solubility curve.

Solubility of mixtures.

When water is shaken with a mixture of two salts, the saturated solution is usually found to contain less of each substance than it would have done had the other been absent, though there are many exceptions to this generalization.

In the case of salts which are not isomorphous and do not form double salts, the composition of the solution is independent of the proportion in which the solids are mixed, and of the method by which the solution is prepared. In the case of substances which form double salts, if we add excess of A to a saturated solution of B, the double salt separates out till a solution is formed which is saturated both as regards A and the double salt, and is not changed by a further addition of A. The third case, when the salts are isomorphous and can crystallize together in all proportions, gives saturated solutions of which the compositions vary continuously with the composition of the solid mixture. By adding successive quantities of A it is possible to completely displace the salt B from the solution. Much experimental work has been done in this subject by Rüdolf[1], and Ostwald has pointed out the analogy between these phenomena and the vapour pressures of mixed liquids, the three cases given above corresponding to the cases (i) when

[1] *Pogg. Ann.* CXLVIII. pp. 456, 555, 1873; *Wied. Ann.* XXV. p. 626, 1885.

the liquids do not mix, (ii) when they are partially miscible, (iii) when they are miscible in all proportions.

Nernst[1] has remarked that the solubility of a slightly soluble salt like silver acetate must be greater in pure water than in a solution of any other electrolyte which contains either silver or the acetate group. A corresponding phenomenon is observed in the case of gases which, like the vapour NH_4SH, decompose to a certain extent. The partial pressures of the products of decomposition are less in the presence of either ammonia or sulphuretted hydrogen.

Solubility in mixed liquids.

On adding a liquid to a solution with which it is miscible, the dissolved substance will be to some extent precipitated if it is insoluble in the liquid added. Thus copper sulphate or sodium chloride can be precipitated from their aqueous solutions by the addition of a certain quantity of alcohol. No relation is yet known between the amount precipitated and the quantity of alcohol added.

A dissolved body divides between two solvents in a constant ratio which is independent of the absolute concentration. This statement was verified for the solution of succinic acid in ether and water by Berthelot and Jungfleisch[2]. If the bodies have different molecular weights when dissolved in the two solvents, like benzoic acid in benzene and water, other laws hold good and have been investigated by Nernst[3].

Tables of solubility.

Full tables of the solubilities of inorganic substances will be found in *A Dictionary of Chemical Solubilities*, by A. M. Comey, 1896. Data will also be found in Watts' *Dictionary of Chemistry*, Roscoe and Schorlemmer's *Chemistry*, and other similar works. The following selection of common substances has been made principally from the first-named book. The solubilities of solids are given in parts by weight of solute in 100 parts of water, but some of those of gases are expressed in terms of the volume of gas, reduced to 0°, which dissolves in 100 volumes of water.

[1] *Zeits. f. physikal. Chemie*, IV. 372, 1889.

[2] *Ann. de Chemie*, XXVI. pp. 396, 408, 1872, [4].

[3] *Zeits. f. physikal. Chemie*, VIII. p. 110, 1891.

Table of Solubilities in Water.

Solute	Solid	At 0°	At 20°	At 100°	Observer	Reference
Ammonia		89·9	51·8	7·4	Sims	Lieb. Ann. **118.** 345
Ammonium chloride	$NH_4.Cl$	29·7	37·2	77·3	Mulder	Scheih. Verh. 1864, 57
Barium chloride	$BaCl_2.2H_2O$	30·9	35·7	58·8	Mulder	Scheih. Verh. 1864, 45
Calcium chloride	$CaCl_2.6H_2O$ etc. etc.	49·6	74	154 (99°)	Mulder	Scheih. Verh. 1864, 107
	$CaCl_2.4H_2O$		103·3 (at 18°·4)		Roozeboom	Rec. des Trav. **8.** 1
	$CaCl_2.2H_2O$			156·5 (95°·8)	Roozeboom	
Calcium carbonate	$CaCO_3$	·0018		·0018	see Roscoe	Vol. II. 1. 208
			·0012		Holleman	Zeit. phys. Ch. **12.** 125
Carbon dioxide		179·7 (vols. at 0°)	90·14 (vols. at 0°)		Bunsen	Gasometry, p. 287 etc.
Copper sulphate	$CuSO_4$	15·5	22·0	73·5	Mulder	Scheih. Verh. 1864, 79
Hydrogen		2·03 (vols. at 0°)	1·77 (vols. at 0°)	1·66 (vols. at 0°)	Bohr & Boch	Wied. Ann. **44.** 318
Hydrogen chloride		82·5	72·1		Roscoe & Dittmar	Lieb. Ann. **112.** 334
Hydrogen sulphide		4·371	2·905		Schönfeld	Lieb. Ann. **93.** 26
Mercurous chloride	Hg_2Cl_2		·00031 (18°)		Kohlrausch & Rose	Zeit. phys. Ch. **12.** 241
Mercurous sulphate	Hg_2SO_4	0·2 (cold)		0·33 (hot)	Wachenroder	Lieb. Ann. **41.** 319
Nitrogen		2·35 (vols. at 0°)	1·54 (vols. at 0°)	0·95 (vols. at 0°)	Winkler	Ber. **24.** 3606
Oxygen		4·89 (vols. at 0°)	3·10 (vols. at 0°)	1·70 (vols. at 0°)	Winkler	Ber. **24.** 3609
Potassium chloride	KCl	28·5	34·7	56·6	Mulder	Scheih. Verh. 1864, 41
Potassium nitrate	KNO_3	13·3	31·2	247	Mulder	Scheih. Verh. 1864, 89
Silver nitrate	$AgNO_3$	121·9	227·3 (19°·5)	1111 (110°)	Kremers	Pogg. Ann. **92.** 497
Sodium chloride	NaCl	35·7	36·0	39·8	Mulder	Scheih. Verh. 1864, 37

CHAPTER V.

OSMOTIC PRESSURE.

Semi-permeable membranes. Osmotic pressure and vapour pressure. Perfect semi-permeable membranes. Theoretical laws of osmotic pressure. Osmotic pressure and heat of solution. Experimental measurements of osmotic pressure.

Semi-permeable membranes.

THE passage of liquids through animal and vegetable membranes has long been a subject of study owing to its bearing on physiological problems. If the mouth of a glass vessel filled with one liquid be closed by a membrane and immersed in some other liquid which passes more freely than the first liquid through the membrane, a pressure will be produced within the vessel until, by the slow processes of diffusion, the composition of the liquids inside and outside has become identical. If a membrane could be obtained which was quite impervious to one of the liquids, it is clear that this excess of pressure would be permanently kept up. The possibility of preparing such membranes was first suggested by Traube[1], as the result of experiments on the methods of formation of organic cells. Solutions of certain substances, which precipitate each other, form insoluble pellicles when brought into contact; these are at all events nearly impermeable to the solutions forming the precipitate and to some other substances.

Pfeffer[2] made a further study of these semi-permeable membranes, and measured the pressures obtained by their

[1] *Archiv f. Anat. u. Physiol.* p. 87, 1867.

[2] *Osmotische Untersuchungen*, Leipzig, 1877.

means. The most usual method of preparing them is as follows. A porous pot of unglazed earthenware, six to eight centimetres high and two or three centimetres in diameter, has a glass tube, which just fits inside it, hermetically sealed to the top by means of sealing wax (Fig. 36). Having been thoroughly washed, it is filled with the solution of a salt such as potassium ferrocyanide, and the outside is then surrounded with the solution of another salt such as copper sulphate or ferric chloride, which gives an insoluble precipitate when in contact with the first salt. The two solutions gradually diffuse from opposite sides into the walls of the cell, and form an insoluble membrane over the surface on which they meet. The solutions are then washed away, and the wide glass tube is drawn out and sealed to a smaller one in the manner shown in the figure.

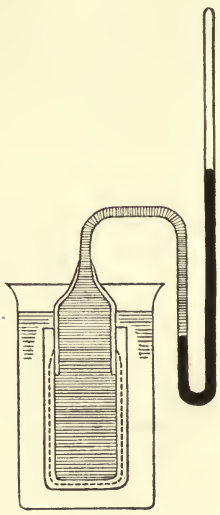


Fig. 36.

Inside a cell thus prepared let us place the solution of some substance such as sugar in water, and surround the outside with a large volume of the pure solvent. Water will gradually enter the cell, and, by using the glass tube as a pressure gauge, it will be found that this influx will continue until a definite internal pressure is reached. This gives a measure of what is called the osmotic pressure of the solution as it finally exists in the cell.

If the membrane has been well prepared, very little if any sugar will escape to the outside, and, although some simple salts and acids will often leak through to some extent, there seems little reason to doubt that membranes can be obtained which are practically impervious to solutions of complex chemical substances such as sugar. At first sight the obvious explanation appears to be that the membrane allows molecules of water to pass, but will not let through molecules of sugar. There is an experiment described by Pickering[1] which suggests

[1] *Ber. Deut. Chem. Ges.*, XXIV. 3639 (1891).

another possible view. If a mixture of propyl alcohol and water be placed in a semi-permeable vessel and surrounded with water, it is found that water enters the cell, and no alcohol escapes. If, however, the same vessel with its same contents be placed in propyl alcohol, it is the alcohol which passes through and enters the vessel, while no water escapes. In this case it seems clear that the membrane is permeable to either water or propyl alcohol when pure, but is impervious to the combination of the two. Further experimental evidence is needed to decide whether or not similar phenomena occur with other solutions. The question is of great interest from its bearing on the problem of the fundamental nature of solution.

The mechanism of the passage of the liquid through the membrane is not fully understood. It may be a purely physical process dependent on the relative sizes of the molecules in the solution and the pores of the membrane, which in this case must be likened to an excessively fine sieve. On the other hand it is possible that loose chemical compounds are formed between the membrane and the solvent, and that these compounds, gradually saturating the membrane, again decompose on its other side where the concentration of the solvent is less.

Another possible explanation depends on the difference in surface tension which may exist between the membrane and the solution or the solvent. In order to see how this may affect matters, we must remember that the existence of surface tension adds a term to the expression for the energy of any body proportional to the area of its surface. A body free from the action of other forces, such as a drop of rain or melted lead falling freely, will therefore assume the shape which makes this energy a minimum, that is, each drop becomes a sphere, the figure having the smallest area for a given volume. Similarly any change which causes a decrease in this portion of the energy of a system will, if it does not increase other parts of the energy, tend to occur. Now the surface tension of salt solutions is different from that of pure water. As usually measured, by capillary tubes, etc., it is the surface tension

of the surface in contact with air, and, for solids which are wetted by the solution, the conditions of equilibrium at the line of contact of solid, liquid and air show at once that as this air tension increases, the surface tension between the liquid and the solid must decrease. It has been found that for most salt solutions, at any rate, the air tension is greater than for water; wherefore the surface tension with which we are concerned must be less. The surface energy of a solid in contact with a solution is therefore less than with pure water, and thus the layer of liquid in contact with the solid will become richer in salt than the bulk of the solution[1]. As the solution flows through capillary tubes, the salt will collect along the walls, and the faster moving central regions will have their concentration diminished. The effect is, that the liquid which finally comes through is pure water. Thus J. J. Thomson and Monckman filtered potassium permanganate from its solution by passage through finely divided silica. The same thing can be seen by allowing dilute permanganate solution to run up into filter paper. The furthest regions reached by the liquid are colourless.

Similar considerations may explain the behaviour of semi-permeable membranes. If they consist of tubes of molecular dimensions, the observed pressures could perhaps be obtained by differences in the surface tensions. At these dimensions, however, the usual principles of capillary action may cease to apply, the distinction between chemical and physical processes may break down, and all these suggested explanations may merely represent different aspects of the same thing.

However this may be, the facts remain, and are of the greatest importance in the theory of our subject.

Osmotic pressure and vapour pressure.

Besides natural membranes and the artificial ones which we have described, there is a semi-permeable diaphragm of the simplest and most perfect kind, consisting of the free surface of a volatile liquid in which some non-volatile substance is dissolved. The solvent in the form of vapour can pass in or out, but the solute is com-

[1] J. J. Thomson, *Applications of Dynamics to Physics and Chemistry.*

pletely confined to the lower side of the surface. If the solvent were non-volatile and the solute a volatile gas, we should get the converse case, in which the solute can pass, but the solvent is confined to the lower side of the diaphragm.

Let us imagine that a tall cylinder containing a solution is placed in an exhausted chamber which also contains a vessel filled with the pure solvent. The vapour pressure of the solvent being higher than that of the solution, liquid will evaporate from the solvent and condense on the solution, the level of which will therefore rise. The concentration of the solution tends to become uniform throughout by diffusion of the solute, and this process can be quickened and made complete at any instant by stirring the liquid. Distillation will then continue, and as the liquid condenses in the cylinder the height of its surface will rise. But the higher we go in the exhausted chamber, the less becomes the pressure of the vapour of the solvent which fills it, just as the pressure of the atmosphere grows less as we ascend. Thus, in the end, the vapour pressure at the surface of the solution becomes equal to that at the same level in the space outside it, and equilibrium results. The difference in pressure between the level of the solvent and that of the solution is equal to the weight of a column of vapour of unit cross section and height h, where h is the difference in level. If we assume the density, σ, of the vapour to be uniform, which involves the assumption that the solution is very dilute, and consequently that the height h is small, the difference in pressure can be written

$$p - p' = h\sigma g.$$

The lowest layer of solution is now under the pressure of the column of solution above it, so that, if the density of the solution is ρ, the hydrostatic pressure at the bottom of the column is

$$P = h\rho g.$$

Now imagine the bottom of the cylinder containing the solution to be put in connexion with the pure solvent through a semi-permeable membrane. There must still be equilibrium, for otherwise, liquid would enter or leave, the height of the

column increase or diminish, and evaporation or condensation occur to compensate for this change. An automatic circulation which could yield an unlimited supply of work would thus be maintained in an enclosure which was originally at a uniform temperature throughout—a process the possibility of which is contrary to experience as formulated in the second law of thermodynamics. It therefore follows that, in the apparatus described, no passage of liquid through the semi-permeable membrane can occur, and thus the hydrostatic pressure at the diaphragm must be equal to the osmotic pressure. The osmotic pressure of the dilute solution of a non-volatile substance is therefore connected with the lowering of vapour pressure in the simple manner expressed by the equation

$$p - p' = P\frac{\sigma}{\rho}.$$

It seems that this result can be extended to the case of volatile solutes, for if we imagine the surface of the solvent to be covered with a membrane permeable to the vapour of the solvent but not to that of the solute, the pressure of the solvent vapour will be everywhere independent of the presence of the solute, and equilibrium will still exist as described.

As FitzGerald indicated[1], the relation between the vapour pressure of a solution and its surface tension is of importance in this connexion. It is well known that water will rise in a capillary tube which is wetted by the liquid, the upper surface being concave upwards, and the angle of contact with the tube zero. The weight of the column of liquid is $h\pi r^2(\rho - \sigma)g$, where r is the radius of the tube, or the radius of curvature of the surface, ρ is the density of the liquid and σ that of the atmosphere surrounding it, which we will suppose to be its own vapour[2]. This weight is supported by the upward pull of the surface tension S between the liquid and the vapour, which acts across each unit of length of the circumference of the tube

[1] Helmholtz Lecture, *Trans. Chem. Soc. Lon.* Jan. 1896.

[2] Lord Kelvin, quoted in Maxwell's *Heat*, 5th ed. p. 290. See also J. J. Thomson, *Applications of Dynamics to Physics and Chemistry*, pp. 163, 164.

where it is touched by the free surface of the liquid, and is therefore $2\pi rS$. Thus

$$2\pi rS = h\pi r^2 (\rho - \sigma) g,$$

or

$$h = \frac{2S}{rg(\rho - \sigma)}.$$

When there is equilibrium, it is evident from Fig. 37 that the vapour pressure from the flat surface of the bulk of the liquid A is greater than that from the concave surface in the capillary by the weight of the column of vapour $h\sigma g$. The decrease of vapour pressure due to the concavity is $2S\sigma/r(\rho - \sigma)$, or, since σ is small compared with ρ, $2S\sigma/r\rho$.

Now, by choosing the tube of the right diameter, we can obviously reduce the vapour pressure of a solvent in it till it sinks to the value of the vapour pressure of a given solution. The difference in vapour pressure of the solvent and solution is $P\sigma/\rho$, where, as we saw, P is equal to the osmotic pressure. Thus,

$$\frac{2\sigma S}{r\rho} = P\frac{\sigma}{\rho},$$

or,

$$P = \frac{2S}{r},$$

an equation which gives the osmotic pressure of a solution having the same vapour pressure as the solvent has in the given capillary tube.

If we have a tube which is not wetted by the liquid, the solution B will sink in it instead of rising and the free surface will be convex instead of concave.

Outside a convex surface the vapour pressure is increased by an amount again given by the expression

$$\frac{2\sigma}{\rho - \sigma} \cdot \frac{S}{r}.$$

By properly choosing the diameter of the tube, remembering that the angle of contact now has a finite value, and placing the tube in the solution instead of the solvent, it is possible to obtain the reverse process, and increase the vapour

pressure of the solution by capillary means till it is equal to that of the solvent.

In Fig. 37, the conditions represented are those of equilibrium. The vapour pressure at the concave surface in the capillary rising from the solvent A is equal to that from the flat surface of the solution B at the same level, and the vapour pressure at the convex surface of the depressed solution B in the unwetted capillary at its side is equal to the vapour pressure of the flat surface of the solvent A at the same level.

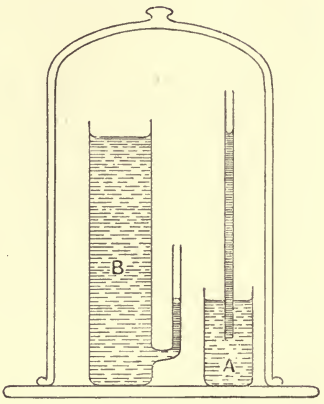


Fig. 37.

Thus vapour pressure, surface tension and osmotic pressure stand in an intimate connexion with each other, which can be traced by the principles of thermodynamics.

Perfect semi-permeable membranes.

The phenomena of surface tension are of theoretical importance in yet another way. The artificial membranes prepared by precipitation often allow solutions of simple salts such as the chlorides of sodium or potassium to leak through them. Although they seem impervious to sugar and similar substances, as far at least as experiment shows, this leakage indicates that they are not perfect. Now the chief importance of osmotic pressure from a theoretical point of view is the possibility it secures of the adaptation of thermodynamic reasoning to the case of solutions. But in doing so, we have to assume (1) that the diaphragms are completely impervious to the solute, (2) that the processes involved in using them are strictly reversible and that no irreversible heat effects occur in them when solvent is passed through. We know too little about the mechanism of the passage of liquids through semi-permeable membranes to be sure that it is not accompanied

by some change in the structure of the walls which may eventually destroy them. Any such effect would render the transfer a non-reversible process and invalidate thermodynamical reasoning based on the second law except as giving an ideal limit which might never be practically realized. It becomes, therefore, of the utmost importance to imagine some diaphragm which is a perfect semi-permeable membrane and can be confidently used hypothetically for the purposes of thermodynamical investigation.

Now, in the arrangement shown in Fig. 37, the vapour from the depressed surface of the solution B in the unwetted capillary is in equilibrium with the vapour of the flat surface of the solvent A at the same level. If the solvent be volatile and the solute perfectly non-volatile, solvent can freely pass as vapour from one vessel to the other, while the solute cannot pass at all. Another method of getting the same result is as follows. Let a plate of some substance which is not wetted by the solution be pierced by a number of capillary tubes, and placed on the surface of the solution. Pressure must be applied before the liquid will rise in the tubes, and, by making the tubes of the right diameter, we can arrange that the curvature of the surface of the solution in them is just enough to increase the vapour pressure to an equality with that of the flat surface of the pure solvent. There will then be equilibrium between the flat surface of the solvent and the solution held in the capillaries, and FitzGerald has pointed out that such an arrangement furnishes a perfect semi-permeable membrane for a non-volatile solute in a volatile solvent[1].

Theoretical Laws of osmotic pressure.

Van 't Hoff showed that the application of thermodynamics enables us to deduce from the observed existence of osmotic pressure its absolute value and the laws which describe its variation with volume and temperature[2]. We shall here treat this problem by an application of the principle of available energy.

[1] Helmholtz Lecture, *Trans. Chem. Soc. Lon.* Jan. 1896.

[2] *Phil. Mag.* vol. xxvi. p. 88, 1888.

Let a volume of the solution of a volatile gas in a non-volatile solvent be confined between two semi-permeable pistons in an engine cylinder. Of these pistons, the upper BB' is permeable to the gas but not to the solvent, the lower CC' is permeable to the solvent but not to the dissolved gas. Two non-permeable pistons AA' and DD' are placed beyond the region occupied by the solution and confine a volume of gas above and a volume of pure solvent below.

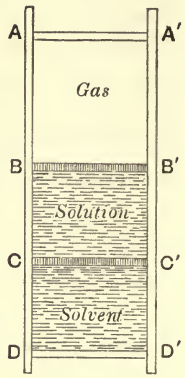


Fig. 38.

Let us at first confine ourselves to the consideration of solutions so dilute that the volume and thermal changes on further dilution are negligible. The piston BB', which defines the top of the solution, can then be fixed, as the total volume of the solution and solvent together is constant.

First, let the pistons AA', DD' also be fixed, so that the whole system is at constant volume, and let the moveable partition CC' have taken up such a position that there is equilibrium between the gas and solution, and between the solution and solvent.

The hydrostatic pressure on the piston CC' must then be equal to the osmotic pressure in the solution (p. 100), while the gas is at the pressure determined by its solubility relations, which for many gases are those described by Henry's law (p. 85), equilibrium being reached when as many molecules enter the solution per second as leave it.

Now when the outside pistons AA', DD' are fixed, the system is at constant volume. The condition of equilibrium then is that the internal thermodynamic potential, or the ψ function, should be a minimum.

For isothermal changes (p. 23, equation 8),

$$\delta\psi = \Sigma(X\,\delta x),$$

and when ψ is a minimum, $\delta\psi$ must vanish, so

$$\Sigma(X\,\delta x) = 0.$$

Now $\Sigma(X\,\delta x)$ denotes the external work, which can be

obtained from the system during an infinitesimal, isothermal, reversible change in the external co-ordinates. Thus under the condition of constant volume of the system the piston CC' will take up such a position that for a small displacement the work obtainable vanishes.

Now if the piston AA' be allowed to rise reversibly, gas will come out of the solution and its osmotic pressure will therefore fall. The hydrostatic pressure below will therefore cause the piston CC' to rise. Besides the external work done or absorbed by the piston AA', external work can also be obtained from or given up to the piston CC' by connecting it with a rod running through the solvent and the wall DD'.

If a volume δv of gas be forced out of a volume δV of solution, the work done by the gaseous pressure on the piston AA' is $p\,\delta v$, and that done against the osmotic pressure by the piston CC' is $P\,\delta V$, so that

$$p\,\delta v - P\,\delta V = 0,$$

or,

$$p\,\delta v = P\,\delta V.$$

By continuing the upward movement of the piston CC' under the constant pressure P, equal to the osmotic pressure, till the whole original volume V of the solution has disappeared, gas will be forced out of solution into the upper space, and the piston AA' will rise under a constant pressure p. This process can be continued till the whole of the dissolved gas is forced out of solution, and occupies a volume v. Both the pressures P and p keep constant throughout the whole operation. Thus the last equation becomes

$$pv = PV,$$

an equation which must hold good at any temperature.

Thus the osmotic pressure of a volatile substance in dilute solution must obey the same volume and temperature relations as does gaseous pressure, and have the same absolute value as the pressure the same number of molecules would exert in an equal volume as a gas[1].

Another simple proof of this identity has been put in the

[1] For a discussion of the subject, see Larmor, *Phil. Trans.* A. cxc. 205, 1897.

following form by Lord Rayleigh[1]. Let us suppose for simplicity that we have an involatile liquid solvent, that its volume is unaltered by dissolving in it a quantity of a certain gas and that the heat of dilution is negligible. The latter suppositions will again limit the strict accuracy of our result to the case of dilute solutions.

We begin with a volume, v, of the gas under a pressure, p_0, and with a volume, V, of the liquid just enough to dissolve the gas under the same pressure. If we bring the gas at pressure p_0 into contact with the liquid, we get an irreversible process of solution; but by expanding the gas we can increase its rarity until no sensible dissipation of energy occurs when contact with the liquid is established. The gas is then gradually compressed and solution goes on under rising pressure until just as the gas disappears the pressure rises to p_0. By conducting the operations at constant temperature, and so slowly that the conditions never deviate sensibly from those of equilibrium, the process can be made reversible.

In order to calculate the amount of work in accordance with the laws of Boyle and Henry, we may conveniently imagine the liquid and gas to be confined under a piston in a cylinder of unit cross section. During the expansion, contact is prevented by a partition inserted at the surface of the liquid. If the distance of the piston from this surface be x, we have initially $x = v$. At any stage of the expansion (x) the pressure, p, is given by $p = \frac{p_0 v}{x}$, and the work gained during the expansion is

$$p_0 v \int_v^x \frac{dx}{x} = p_0 v \log \frac{x}{v},$$

x being large compared with v. The partition is then removed and during the condensation the pressure upon the piston in a given position x is less than before, for the gas is now partly in solution. If s denote the solubility, the available volume is practically increased in the ratio $x : x + sV$, so that the pressure in the position x is now

$$p = \frac{p_0 v}{x + sV},$$

[1] *Nature*, vol. LV. p. 253, 1897.

and the work done during the compression is

$$p_0 v \int_0^x \frac{dx}{x+sV} = p_0 v \log \frac{x+sV}{sV}.$$

On the whole the work lost during the two operations is

$$p_0 v \left\{ \log \frac{x+sV}{x} + \log \frac{v}{sV} \right\},$$

and of this the first term can be neglected as x is indefinitely great. Since by supposition the quantity of liquid is such as to be just capable of dissolving the gas, $sV = v$ and the second term also is equal to zero. The gas has therefore been dissolved reversibly without gain or loss of work.

In order to complete the cycle, we must remove the gas from solution and bring it to its original state by an application of the osmotic process of Van 't Hoff. One semi-permeable membrane, permeable to the gas but not to the liquid[1], is introduced just under the piston which rests at the surface of the liquid. A second, permeable to liquid but not to the gas, is substituted as a piston for the bottom of the cylinder and is in contact with pure solvent on its lower side. By suitable motions of the two pistons, the upper one being raised through the space v and the lower through the space V, the gas may be expelled at a constant pressure, p_0; the solution which remains will keep a constant strength and therefore a constant osmotic pressure which we will call P. When the expulsion is complete the work done on the lower piston is PV and that done by the gas is $p_0 v$. Thus the whole work done is $PV - p_0 v$, and this process as well as the first is reversible.

Since the whole cycle has been conducted at constant temperature, it follows from the second law of thermodynamics that on the whole no work is gained or lost. Thus,

$$PV - p_0 v = 0 \text{ or } PV = p_0 v.$$

The osmotic pressure P is thus determined, and it is evident that its value is equal to that of the pressure which the gas, as a gas, would exert in a space V.

[1] The upper surface of an involatile liquid may itself be considered as such a membrane.

This cycle could be performed at any temperature, and it must therefore follow that the temperature variation of the osmotic pressure of a dilute solution of constant concentration must be the same as that of a perfect gas. For dilute solutions, therefore, the osmotic pressure should be proportional to the absolute temperature.

We have thus theoretically proved, without any assumption as to the real nature of a solution, that the laws of osmotic pressure are, for dilute solutions of volatile bodies, the same as those of gases. We may therefore collect our results in a form equivalent to the usual "gas equation" and write

$$PV = mRT,$$

m denoting the number of gram-molecules considered, and the constant R having the same value as for gases.

The extension of this theorem to the case of solutions of metallic salts and other substances not appreciably volatile involves a certain amount of assumption. It seems reasonable to suppose, however, that the distinction is one of degree rather than of kind, bodies of almost every grade of volatility being known. There is thus evidence to show that the results of the thermodynamic considerations we have given hold good for all solutions, and that the osmotic pressure of even non-volatile solutes has the same value as an equal number of molecules would exert could they be gasified and confined in the same volume.

Another point which must be noticed is the fact that the proofs assume that there is no change in the state of molecular aggregation as the solute is expelled from solution: that the same amount of substance yields the same number of integrant particles in each condition. Thus, if dissociation or association occurred either in the gaseous or the liquid state, the pressure exerted in that state would be changed to a corresponding amount. The importance of this remark in the case of electrolytes will be evident later on, when we shall find that such bodies give abnormally high osmotic pressures if dissolved in water.

It will be noticed that these deductions of the osmotic

relations depend on the experimental result that the mass of gas in solution depends on its gaseous pressure. But the theory of osmotics can be placed on an abstract basis independently of the law of the solubility of gases, which could then be deduced from it. The principles involved were laid down in a general manner by Gibbs as early as 1875[1], and were also used in the equations given by von Helmholtz in 1883[2], in a discussion of the energy relations of gases in connexion with the theory of galvanic polarization, which will be considered in a later chapter. The argument has been applied in a definite form to the problem in hand by Larmor, as quoted below[3].

Whatever the exact physical connexion between the solute and the solvent may be, "each molecule of the dissolved substance forms for itself a *nidus* in the solvent, that is, it sensibly influences the molecules around it up to a certain minute distance so as to form a loosely connected complex, in the sense not of chemical union but of physical influence. The laws of this mutual molecular influence are unknown, possibly unknowable; but provided the solution is so dilute that each such complex is, for very much the greater part of the time, out of range of the influence of the other complexes, as for instance are the separate molecules of a free gas, then the principles of thermodynamics necessitate the osmotic laws. It does not matter whether the nucleus of the complex is a single molecule, or a group of molecules, or the entity that is called an ion: the pressure phenomena are determined merely by the number of complexes per unit volume. To determine the osmotic forces, we must know the change in *available* energy that is involved in dilution of the solution by further transpiration of the pure solvent into it. In finding that change, the laws of mutual action between molecules of the dissolved substance are not required: for there is actually no action between them, and as soon as the solution becomes so concentrated that such mutual action between the complexes

[1] *Trans. Connect. Acad.* III. 138 (1875): (Equilibrium of Osmotic Forces).

[2] *Abhandlungen*, III. 101 (1883).

[3] *Proc. Cambridge Philos. Soc.* IX. 240 (1897); *Phil. Trans.* A. CXC. 205 (1897).

comes in, the theory is no longer exact. Nor are the laws of mutual action between the molecules of the dissolved substance and those of the solvent required, because the effect of transpiration of more of the solvent into the solution is not in any way to alter the individual complexes. The change in available energy of the system, on dilution, thus solely arises from the expansion of the complexes into a larger volume; and it can be traced into exact correlation with the change of available energy that occurs in the expansion of a gas. This argument meets the objection that a true theory should involve a knowledge of the molecular actions between the various molecules. It would seem that with just the same cogency it might be argued that a real investigation of the connexion of the alteration of the freezing point of a liquid by pressure and its change of volume on freezing should involve a knowledge of the individual molecular actions in the liquid: and so it would, had we not the means of evading considerations of molecular constitution that is afforded by Lord Kelvin's great principle of dissipation, which is for this very reason at the basis of all physical theory.

"There is however one point to be remembered, namely, that the theoretical osmotic pressure is a limiting value which may not be reached by an actual arrangement, unless we can be certain that it works reversibly and so without heating effects.

"The remark has been made by Lord Kelvin, that the connexion between Henry's law and the osmotic law must break down when the solution of the gas is accompanied by change in its state of molecular aggregation. It is also probable from the fundamental ideas as to dissociation and aggregation, that such change would usually be partial, and not uniform over all the dissolved molecules; so that it is not to be expected that Henry's law would in such circumstances hold good. The point in which the argument, as set forth in precise form by Lord Rayleigh, becomes then inapplicable, is that the gas expelled from solution by the osmotic process must be considered as emerging in the actual state of aggregation differing from that of its free condition, and its return to the latter state involves further change of available energy."

Thus the similarity between the laws describing the pressure of gases and those holding for the osmotic pressure of dilute solutions does not show that the real cause of these laws is the same in both cases. It simply depends on the fact that, in each, the molecules are so far apart that they are nearly always beyond each other's spheres of action.

The foregoing investigations assume that both the heat of dilution and the change of volume on dilution of the solution considered are small. The results are therefore restricted to dilute solutions. In order to find a general expression giving the relation between the osmotic pressure of a solution and its concentration, let us take the free energy equation (p. 29),

$$\psi = \epsilon + \theta \frac{d\psi}{d\theta}.$$

The free energy is the work obtainable by a reversible and isothermal process, and is thus equal to $-Pv$, P being the osmotic pressure and v the increase in volume of the solution, when solvent is added isothermally and reversibly through a semi-permeable membrane. If the solvent had been added directly in a calorimeter, without a membrane, a certain amount of heat would have been evolved or absorbed in an irreversible manner. For small changes, this heat would be proportional to the increase in volume of the solution, and may thus be written as lv, where l is the heat of dilution per unit change of volume.

In this irreversible process, the internal energy of the system would decrease by an amount lv, the external work being negligible. In the reversible osmotic process, the initial and final states of the system are the same as they are in the irreversible change, and thus the decrease in internal energy must be also the same, and ϵ is $-lv$: we then get,

$$Pv = lv + \theta \frac{\partial (Pv)}{\partial \theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots (13).$$

Thus, in order to deduce the relation between osmotic pressure and concentration, we must experimentally determine the heat of dilution, and also know the rate of variation of the osmotic energy with the temperature.

If we neglect the change of volume with temperature, equation (13) becomes

$$Pv = lv + \theta v \frac{\partial P}{\partial \theta},$$

or

$$P = l + \theta \frac{\partial P}{\partial \theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14),$$

which gives a relation between the osmotic pressure and the heat of dilution of the solution.

If the solution is so dilute that further addition of solvent produces no thermal effect, l is nothing, and the equation becomes

$$\frac{\partial P}{\partial \theta} = \frac{P}{\theta},$$

or, rearranging,

$$\frac{dP}{P} = \frac{d\theta}{\theta}.$$

It can then be integrated and gives

$$\log P = \log \theta + \text{constant},$$

or,

$$P = \theta \times \text{constant},$$

in accordance with our result on p. 108, which shows that, since the osmotic pressure of a very dilute solution always has the same absolute value as the gaseous pressure for the same concentration, it must be proportional to the thermodynamic temperature.

Osmotic pressure and heat of solution.

Let us imagine a saturated solution, in contact with the solid crystals of its solute, to be confined in a cylinder with the bottom formed of a semi-permeable membrane, and immersed in a large volume of the pure solvent. The piston of the cylinder is weighted till the pressure it exerts is equal to the osmotic pressure within the cylinder. The system is then in equilibrium.

By reducing the weight by an indefinitely small amount, the solvent can be made to enter from below and the piston to rise. The osmotic pressure is then performing work. As the solvent enters, more of the solid crystals will dissolve,

keeping up the saturation. This process will, in general, involve a (positive or negative) thermal change, and we must therefore let a (positive or negative) quantity of heat enter to keep the system at a constant temperature.

By increasing instead of diminishing the weight, solvent can be forced out, and the whole process reversed. Thus, by keeping the pressure indefinitely near the osmotic pressure, and making the movements of the piston slow, the changes can be made reversible and isothermal.

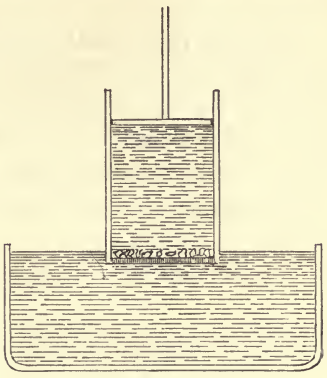


Fig. 39.

In such a case the equation of free or available energy (p. 29)

$$\psi = \epsilon + \theta \frac{d\psi}{d\theta}$$

is applicable, just as it is to the case of the isothermal evaporation of a liquid or fusion of a solid.

When the piston rises and a change in volume of the saturated solution from v_1 to v_2 occurs, the work done is

$$P(v_2 - v_1) = -\psi,$$

where P is the osmotic pressure. Thus the rate of increase of the available energy with the temperature at constant volume is given by

$$\frac{d\psi}{d\theta} = -\frac{dP}{d\theta}(v_2 - v_1).$$

From the definition of ψ on page 23,

$$\psi = \epsilon - \theta\phi,$$

or for reversible changes, when H is equal to $\theta\phi$,

$$\psi = \epsilon - H,$$

ϕ, ψ, ϵ and H denoting finite changes in the values of the usual functions. Thus, the free energy equation gives

$$\psi - \epsilon = -H = \theta \frac{d\psi}{d\theta},$$

or,

$$H = \theta \frac{dP}{d\theta}(v_2 - v_1).$$

If we suppose that the process of solution continues until one gram-molecule of the solid is dissolved, we may write λ' for H, λ' being the heat of solution of one gram-molecule of the solute when dissolved to form the volume, v, of saturated solution in such a manner that the amount Pv of osmotic work is simultaneously performed. The result is the latent heat equation

$$\lambda' = \theta \frac{dP}{d\theta} v \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15).$$

Instead of using the principle of available energy, this relation could have been deduced from the principle of entropy, or directly, by taking the system of cylinder, semi-permeable membrane and solvent through a complete reversible cycle, and writing down the expression for the efficiency of the process. The results expressed in equation (15) show that the rate of change with temperature of the osmotic pressure of a solution, kept constantly saturated, has the same sign as the heat of solution of the solid under the same conditions.

The osmotic pressure of a solution depends on the concentration, and is approximately proportional to it. Thus the value of P in our equation is a function of the concentration of the saturated solutions, that is, of the solubility.

The heat of solution in equation (15) is the heat which must be supplied to keep the temperature constant when one gram-molecular weight of solid is dissolved in a solvent to give a volume v of saturated solution, and a quantity of osmotic work Pv is done. The heat of formation as measured in a calorimeter, however, does not involve the performance of external work, and, since the internal energy of the solution must be the same by whichever process it is made, the difference between these two quantities of heat must be the thermal equivalent of the work done. Thus, in mechanical units,

$$\lambda' = \lambda + Pv.$$

The latent heat equation given above is general, but, if we

limit the investigation to dilute solutions, we can write for one gram-molecular weight

$$Pv = R\theta.$$

The latent heat equation then becomes

$$\lambda' = \theta \frac{dP}{d\theta} \frac{R\theta}{P} = R\theta^2 \frac{dP}{d\theta} \frac{1}{P},$$

or,

$$\lambda' = R\theta^2 \frac{d}{d\theta} (\log_e P),$$

that is,

$$\frac{d}{d\theta} (\log_e P) = \frac{\lambda'}{R\theta^2}.$$

If we make the further assumption that the heat of solution is constant with changing temperature, a supposition which is not far from the truth in many cases for small ranges of temperature, the equation can be integrated to give the result

$$\log \left(\frac{P_2}{P_1}\right) = \frac{\lambda'}{R} \left(\frac{1}{\theta_1} - \frac{1}{\theta_2}\right) \ldots\ldots\ldots\ldots\ldots\ldots (16).$$

The calorimetric heat of formation of the saturated solution λ, is given by

$$\lambda' = \lambda + Pv = \lambda + R\theta$$

for dilute solutions; the osmotic pressure is then

$$P = \frac{R\theta}{v} = R\theta C,$$

where C is the concentration, that is the number of gram-molecular weights of solid dissolved in unit volume of the saturated solution.

The latent heat equation gives, since R is constant,

$$\lambda + R\theta = R\theta^2 \frac{d(\log C + \log \theta)}{d\theta}$$

$$= R\theta^2 \left\{\frac{d}{d\theta} (\log C) + \frac{1}{\theta}\right\},$$

or,

$$\lambda = R\theta^2 \frac{d}{d\theta} (\log C) \ldots\ldots\ldots\ldots\ldots (17).$$

Thus the calorimetric heat of formation of the saturated solution has the same sign as the temperature coefficient of the

solubility, the heat of formation being reckoned positive when heat must be taken in by the system during the process of solution in order to keep the temperature constant.

This heat will not, in general, be the same as the heat of solution in a large volume of the pure solvent, and very often has actually a different sign. Thus cupric chloride and also the hydrates of ferric chloride dissolve in much water with an evolution of heat, but when the solution is nearly saturated, it is cooled by taking up more of one of these solids. Heat must then enter the system to keep the temperature constant while solution is going on, and λ is therefore positive.

We can, from the equation, deduce λ from the solubility curve, but the solubility cannot be deduced conversely from the heat of solution (though its temperature variation can), for if we integrate the equation we get

$$\log C = \int \frac{\lambda d\theta}{R\theta^2} + \text{constant},$$

and this constant, which determines the absolute value of the solubility, remains unknown.

The equation

$$\lambda = R\theta^2 \frac{d}{d\theta}(\log C),$$

however, like the other, can be integrated between limits on the assumption that the variation of λ with temperature can be neglected, and then gives

$$\log\left(\frac{C_2}{C_1}\right) = \frac{\lambda}{R}\left(\frac{1}{\theta_1} - \frac{1}{\theta_2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (18).$$

The osmotic pressure of an electrolyte, as we shall see later, is greater than the normal value, and must therefore be expressed in the form

$$P = iR\theta C,$$

where i denotes the ratio between the actual and the normal pressure. Assuming i to be constant, the equation then becomes

$$\log\left(\frac{C_2}{C_1}\right) = \frac{\lambda}{Ri}\left(\frac{1}{\theta_1} - \frac{1}{\theta_2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (19).$$

In order that the heat of solution and the ratio i should be sensibly constant, temperatures not too far apart must be chosen for experiment. Van 't Hoff, to whom these equations are due, gives a table of experimental verification from which we select the following examples[1]:

	$\frac{\lambda}{1000}$ calculated	$\frac{\lambda}{1000}$ observed
Boric acid	5·8 calories	5·6 calories
Oxalic acid	8·2 „	8·5 „
Potassium bichromate	17·3 „	17·0 „
Amylic alcohol	− 3·1 „	− 2·8 „
Phenol	1·2 „	2·1 „
Alum	21·9 „	20·2 „
Potassium chlorate	11 „	10 „
Borax	27·4 „	25·8 „

For very slightly soluble salts such as barium sulphate, the saturated solutions are so dilute that the ionization may be taken as complete. The heat of solution is equal and of opposite sign to the heat of precipitation. This heat can be measured calorimetrically; for example by treating a solution of barium chloride with one of sodium sulphate; the only change is the precipitation of barium sulphate, for the sodium and chlorine ions remain dissolved and unaffected[2].

	θ_1	$1/C_1$	θ_2	$1/C_2$	λ calᵈ.	λ obsᵈ.
Barium sulphate	18°·4	50055	37°·7	37282	5500	5583
Silver chloride	13 ·8	102710	26 ·5	55120	15992	15850

Experimental measurements of osmotic pressure.

The importance of experiments on osmotic pressure was first pointed out by Van 't Hoff[3], who called attention to the fact that Pfeffer's measurements on cane sugar proved that the pressure varied as the concentration, i.e. that it was inversely proportional to the volume occupied by a given mass of sugar. This exactly corresponds to Boyle's law for gases. The following are some of Pfeffer's numbers as given by Van 't Hoff.

[1] *Kongl. Svenska. Akad. Handl.* xxi. p. 38, 1885.

[2] Lehfeldt's *Physical Chemistry*, London (1899), pp. 270, 271.

[3] *loc. cit.*; *Phil. Mag.* xxvi. p. 81, 1888, or *Zeits. f. physikal. Chemie*, i. p. 481, 1897.

Percentage of sugar in solution	Pressure in millimetres of mercury	Pressure calculated for one per cent. of sugar
1	538	538
1	532	532
2	1016	508
2·74	1513	554
4	2082	521
6	3075	513
1	535	535

The numbers in the last column are constant except for irregular experimental errors.

In the case of gases, Boyle's law fails to represent the accurate relation between pressure and volume at high pressures, and it similarly fails for solutions when the concentration becomes considerable. We should expect the law of variation to be more complicated for solutions, since in addition to intermolecular forces similar to those brought into play in the case of gases, we shall here have forces between the dissolved molecules and the solvent.

As we have seen, the theory shows that the pressure should increase as the temperature rises; and that, for dilute solutions, the variation should follow the laws of gases and make the pressure proportional to the absolute temperature. This result has been examined experimentally by Pfeffer, who gives for cane sugar

t_1	14°·15	P_1	510	t_2 32°	P_2 544
	15°·5		520·5	36°	567

These numbers lead to a mean value for the coefficient of increase of pressure per degree of 1/234 of the pressure at 15°.

Again Donders and Hamburger[1] found that the variation in pressure due to temperature was independent of the nature of the dissolved substance. This corresponds to the fact that the coefficient of increase of pressure is the same for all gases. The method used was a comparative one, and showed that solutions which were isotonic (i.e. gave equal osmotic pressures) at one temperature, 0°, were also isotonic at another, 34°.

The protoplasmic contents of certain organic cells are

[1] *Zeits. f. physikal. Chemie*, VI. p. 319, 1890.

surrounded by a membrane which seems to be very effective in only allowing pure water to pass. If such a cell be placed in a concentrated salt solution, the more dilute cell sap parts with water faster than the external liquid, the contents of the cell contract and shrink away from the cell walls. If on the other hand the cell be placed in water, liquid passes in, and the membrane becomes stretched. By staining the contents of the cell and having a graduated series of solutions of varying strength, it is easy to find, by observations with a microscope, what strength of solution gives equilibrium with the cell sap, and is therefore isotonic with it. Solutions of two different substances can thus be prepared so that both are isotonic with the contents of a given kind of cell, and, assuming that two solutions isotonic with a third are isotonic with each other, we can find the respective strengths of the two salt solutions which give equal osmotic pressures. De Vries[1], who was the first to use this method, employed vegetable cells, and Donders and Hamburger, in their investigation on the influence of temperature, used blood corpuscles.

De Vries established the most important generalization, that solutions of different non-electrolytic substances containing the same number of gram-molecules in a given volume are isotonic. This is equivalent to saying that at equal pressures the solutions of all such substances contain, in a given volume, the same number of molecules, a statement which corresponds to Avogadro's law for gases. Tammann[2] confirmed this by allowing a drop of copper sulphate solution to fall into a solution of a ferrocyanide. A little membrane was at once formed round the drop, and the concentrations of the solutions were altered till, when this was done, no water entered or left the drop. Whether any such passage went on or not was determined by noticing if there was any change in the index of refraction of the liquid just outside the little cell.

It is important to observe that in the case of solutions which are electrolytes (that is to say, which have the power of conveying a current of electricity and of undergoing simulta-

[1] Pringsheim's *Jahrbücher*, XIV. p. 427, 1884.

[2] *Wied. Ann.* XXXIV. p. 299, 1888.

neous chemical decomposition), the osmotic pressure is greater than that given by the solution of a non-electrolyte containing the same number of gram-molecules in a given volume. Thus a table of the "isotonic coefficients" of some indifferent substances given by De Vries is as follows, the isotonic coefficient being a number representing the osmotic pressure when that of an equimolecular solution of potassium nitrate is taken as 3:

Cane sugar	1·81
Inverted sugar	1·88
Glycerine	1·78

while the coefficients of electrolytic solutions are greater:

Potassium nitrate	3·0
Sodium nitrate	3·0
Potassium chloride	3·0
Potassium sulphate	3·9
Potassium tartrate	3·99
Magnesium chloride	4·33
Calcium chloride	4·33

We shall examine this phenomenon in detail in a later chapter.

When we pass on to the examination of the absolute value of the osmotic pressure, we find another striking relation to gaseous properties. We know that one gram of hydrogen or sixteen grams of oxygen, at normal atmospheric pressure and 0° C., occupy a volume of about 11·16 litres. Therefore one molecular weight of a gas in grams (2 grams of hydrogen or 32 grams of oxygen) occupies under these conditions a volume of 22·32 litres, or if compressed into one litre would, by Boyle's law, exert a pressure of 22·32 atmospheres. By Avogadro's law the same pressure would be exerted by any gas or vapour that was a considerable distance from its point of liquefaction. The absolute values of osmotic pressures have been found by Pfeffer, Adie[1] and Tammann. Pfeffer found that at 6°·8 a one per cent. solution of sugar gave an osmotic pressure of 505 mm. of mercury. The molecular weight of cane sugar ($C_{12}H_{22}O_{11}$) is 342. Hence a one per cent. solution contains

[1] *Chem. Soc. Jour. Proc.* p. 344, 1891.

$\frac{10}{342}$ of a gram-molecule in one litre. A volume of hydrogen or of any other gas, which contained $\frac{10}{342}$ of a gram-molecule in one litre would at 6°·8 exert a pressure of

$$760 \times \frac{10}{342} \times 22{\cdot}32 \times \frac{279{\cdot}8}{273} = 508 \text{ mm. of mercury.}$$

Thus we find that in dilute solutions of indifferent substances

(i) The osmotic pressure is proportional to the concentration, that is, inversely proportional to the volume occupied by a given mass (Boyle's law).

(ii) The coefficient of variation of pressure with temperature is the same for all substances, and probably (though this is not fully established by experiment) the pressure is proportional to the absolute temperature (Gay Lussac's law).

(iii) Solutions which exert the same pressures contain the same number of dissolved molecules in a given volume (Avogadro's law).

(iv) The absolute value of the osmotic pressure of the solution of a non-electrolyte is the same as that of a gas or vapour containing the same number of molecules in a given volume.

Hence we find that the osmotic pressure of dilute solutions obeys all the gaseous laws, and has the same absolute value as it would have if the dissolved substance were transformed into a gas at the same temperature and confined in the same volume. Thus, the gaseous laws which we deduced theoretically for dilute solutions of volatile substances are also established by direct experiment for non-volatile solutes.

The direct determination of osmotic pressure is a very difficult process, but we shall show that there is a connection between this pressure and other properties of solutions—their vapour pressures, and freezing points. This connection is independent of the particular view we take of the cause of osmotic pressure, and can be deduced simply from the principles of thermodynamics. For most purposes, therefore, it is better to make an experimental determination of the freezing point, and deduce the corresponding value of the osmotic pressure.

CHAPTER VI.

VAPOUR PRESSURES AND FREEZING POINTS.

Connection with osmotic pressure. The latent heat equation. The depression of the freezing point. Vapour pressures of concentrated solutions. Solubility of gases in liquids. Experimental measurements of vapour pressures. Boiling points. Determination of molecular weights. Freezing points. Osmotic pressure and freezing points of concentrated solutions. Experiments on the freezing points of solutions. Determinations of molecular weights.

THE phase rule enables us to trace all the qualitative phenomena of the equilibrium of a solution with its possible gaseous and solid phases, but, in certain cases, a more detailed study of both the theory and the experimental investigation of the quantitative relations is possible.

Connection with osmotic pressure.

There is an intimate connection between the osmotic pressure of a solution, its freezing point and the saturation pressure of its vapour at a given temperature on which its boiling point obviously depends.

Let us suppose that two vessels, one of which contains a solution of a non-volatile substance and the other pure water, are placed side by side under an exhausted bell-jar. Since the vapour pressure of the solution is less than that of the water, distillation from one to the other will occur and the level of liquid in the vessel which contains the solution will rise. If the solution be kept stirred, this process will go on until each liquid is in equilibrium with the vapour lying in contact with it. The difference in pressure of the vapour at these two levels will be

equal to the weight of a column of the vapour equal in height to the difference between the heights of the two columns of liquid. Thus, if p be the vapour pressure of the solvent at the temperature of the experiment, and p' that of the solution, if σ be the density of the vapour, which we will at first assume uniform, and h be the difference in level of the two columns of liquid, which we must then take to be small, we get the equation

$$p - p' = g\sigma h.$$

The hydrostatic pressure in the solution at the level of the water is

$$P = g\rho h,$$

where ρ is the density of the solution. Thus

$$p - p' = \frac{P\sigma}{\rho} \quad \text{.....(20).}$$

Here σ is the density of the vapour under its own pressure; if σ_0 be its density under the pressure of the standard atmosphere A, σ is $\sigma_0 p/A$, and

$$p - p' = \frac{P\sigma_0 p}{A\rho}$$

or

$$\frac{p - p'}{p} = \frac{P\sigma_0}{A\rho} \quad \text{.....(21).}$$

The bottom of the solution vessel can now be replaced by a perfect semi-permeable membrane such as is described on p. 103, and put into connexion with the pure solvent; equilibrium will still exist, for if not, water will enter or leave the solution, its level will change, the equilibrium with the vapour be upset and a constant circulation go on in an originally isothermal enclosure, a state of things which, contrary to experience, would allow an unlimited supply of mechanical work to be obtained. Thus P can be taken as denoting the osmotic pressure of the solution, and we have a relation between it and the lowering of the vapour pressure.

The freezing point of a solution is lower than that of the solvent if the solid which separates is the ice of the pure solvent, and it is easy to show that the vapour pressure of the

solution at its freezing point is the same as that of the ice of the solvent at the same temperature.

Let us imagine the system put through the following isothermal and reversible cycle, all the operations being performed at the freezing point of the solution. (1) Evaporate some solution, (2) compress or expand the vapour if necessary until it is in equilibrium with the solid of the pure solvent, (3) condense this vapour on to the solid, (4) allow the same mass of solid to melt in contact with the solution. This is a complete reversible isothermal cycle, and therefore no work is, on the whole, done.

Let p' and p'' be the vapour pressures of the solution and solid respectively, v the volume of vapour at pressure p', and v' its volume when the pressure is p''.

In process (1) an amount of work $p'v$ is done by the vapour, in (2) the work $\frac{p'+p''}{2}(v-v')$ is done on it, in (3) $p''v'$ is done on it and in (4) no work is done.

Equating the total work to zero

$$p'v - \frac{p'+p''}{2}(v-v') - p''v' = 0.$$

The pressures involved are small, and during the second operation the vapour considered is not saturated and therefore the change may be taken as described by Boyle's law.

Thus

$$p'v = p''v'.$$

Therefore

$$\frac{p'+p''}{2}(v-v') = 0.$$

But $\frac{p'+p''}{2}$ is a finite quantity, therefore

$$v = v',$$

and, by the Boyle's law relation,

$$p' = p'',$$

that is, the vapour pressure of the solution at its freezing point is the same as the vapour pressure of the solid of the pure solvent at the same temperature.

The latent heat equation.

We have seen that when a change of state is going on, the relation of pressure to temperature at constant volume can be described by the differential equation

$$\frac{dp}{d\theta} = \frac{\lambda}{\theta(v_2 - v_1)}.$$

If we confine ourselves at first to dilute solutions, the freezing points will only differ from that of the pure solvent by a very small amount. In Fig. 40, then, which represents the equilibrium of the three phases of the pure solvent, solid, liquid and vapour, we need only consider the immediate neighbourhood of the triple point, T. The curve DTB denotes the vapour pressure of the liquid solvent, the part DT relating to the undercooled liquid, while the curve TC gives the vapour pressure of the solid.

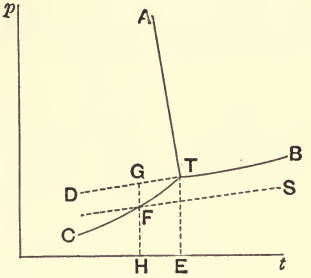


Fig. 40.

Along these two curves the equation may be written as

$$\frac{dp}{d\theta} = \frac{\lambda_{lv}}{\theta(v_v - v_l)} \text{ and } \frac{dp}{d\theta} = \frac{\lambda_{sv}}{\theta(v_v - v_s)},$$

or, since we can neglect the small volumes of the liquid (l) or solid (s), as compared with the large volume of the vapour,

$$\delta p_l = \delta\theta \frac{\lambda_{lv}}{\theta v} \text{ and } \delta p_s = \delta\theta \frac{\lambda_{sv}}{\theta v}.$$

Subtracting one of these equations from the other, and remembering that, at the triple point, the latent heat of the change from solid to vapour must be the sum of the latent heats from solid to liquid and from liquid to vapour, we have

$$\delta p_s - \delta p_l = \frac{\delta\theta\lambda_{sl}}{\theta v} = \delta\theta \,.\, \frac{\lambda\sigma}{\theta},$$

where σ is the density of the vapour, and therefore equal to $1/v$, v being the volume of unit mass.

The depression of the freezing point.

Now, as we saw, the vapour pressure of a solution at its freezing point is equal to that of the solid phase of the pure solvent at the same temperature, and thus if we add to Fig. 40 the curve *SF*, giving the vapour pressure of the solution, the point *F* at which it cuts *TC*, the vapour pressure curve of the solid solvent, gives the freezing point of the solution. Now *FG* measures $\delta p_s - \delta p_l$, and also denotes the lowering of vapour pressure of the solution as compared with that of the pure liquid solvent at the same temperature. It is thus equivalent to $p - p'$ in the equation

$$p - p' = \frac{P\sigma}{\rho}.$$

We may therefore write

$$\delta\theta \frac{\lambda\sigma}{\theta} = \frac{P\sigma}{\rho},$$

or

$$\delta\theta = \frac{P\theta}{\lambda\rho} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (22),$$

an equation which gives the connection between the osmotic pressure of a solution and the lowering of its freezing point in the limiting case where the dilution of the solution is pushed to the extreme.

It is usual to obtain this equation by means of a thermodynamic cycle with a system composed of water separated from a solution by means of a semi-permeable membrane, but the above treatment of the problem, pointed out to the author by Professor Poynting, appears somewhat more direct, and has therefore been adopted.

Vapour pressures of concentrated solutions.

The vapour pressure equation

$$p - p' = g\sigma h$$

has been obtained by assuming that the density of the vapour in our exhausted bell-jar is everywhere uniform. Such an assumption is only justified if the column of vapour of height h is short, that is, if the concentration of the solution is exceedingly small. Where this

is not the case, we must divide the height h of the vapour into a number of parts each equal to δh and put

$$\delta p = -g\sigma\delta h,$$

or

$$\delta h = -\frac{\delta p}{g\sigma}.$$

Let σ_0 be the density of the vapour at the pressure, A, of the standard atmosphere, then

$$\sigma = \sigma_0 \frac{p}{A},$$

and

$$\delta h = -A\,\frac{\delta p}{g\sigma_0 p}.$$

By integrating from 0 to h we get

$$h = \frac{A}{g\sigma_0} \log_e \left(\frac{p_0}{p_h}\right),$$

p_0 being the pressure at the level of the water, i.e. the vapour pressure of the pure solvent p, and p_h the pressure at the height h, i.e. the vapour pressure of the solution, p'.

Now

$$h = \frac{P}{g\rho},$$

and therefore

$$\log_e \left(\frac{p}{p'}\right) = \frac{P\sigma_0}{A\rho} \quad \text{.....(23).}$$

This equation gives a necessary relation between the osmotic pressure and the lowering of the vapour pressure of any solution, and is quite independent of any assumption as to the physical nature of osmotic pressure. Be this what it may, we know that osmotic pressure exists, and it therefore follows that the vapour pressure must be lowered by the amount shown in our equation. The value of the osmotic pressure can thus be deduced from observations on the diminution of the vapour pressure, whatever be the concentration of the solution.

It is easy to transform our equations into forms which give the concentration of the solution in terms of the ratio of the number of molecules of dissolved substance to the number of molecules of solvent, which simplifies the comparison with experimental results. If one gram-molecule in a gas or solution fills a volume v_0 at a pressure A, the osmotic

pressure for a concentration of n gram-molecules in a volume v is

$$P = \frac{Av_0 n}{v}.$$

Now the mass of the solvent is NM, where N is the number of gram-molecules and M its molecular weight, and the volume is the mass divided by the density,

or $$v = \frac{NM}{\rho}.$$

Thus $$P = \frac{Av_0 n\rho}{NM}.$$

The density σ_0 of the vapour under normal conditions of temperature and pressure is M'/v_0, where M' is the molecular weight of the solvent in the state of vapour. By substituting in the approximate equation (21)

$$\frac{p - p'}{p} = \frac{P\sigma_0}{A\rho},$$

we get $$\frac{p - p'}{p} = \frac{n}{N} \cdot \frac{M'}{M}.$$

This equation shows that the relative lowering of vapour pressure depends on n, the number of molecules of the solute, but not on N, the number of those of the liquid solvent: if N be changed, M is changed in the inverse ratio, and the value of the expression is unaltered. If the molecular weight M' of the solvent as vapour is equal to M, the value assumed for its liquid in calculating the concentration of the solution in terms of the relative numbers of molecules, the equation becomes

$$\frac{p - p'}{p} = \frac{n}{N} \quad \text{.....(24).}$$

If we treat equation (23), which gives the strict relation with the osmotic pressure, in the same way, assuming as before that P is proportional to the concentration, we get

$$\log_e \left(\frac{p}{p'}\right) = \frac{n}{N} \quad \text{.....(25).}$$

Both the ratios $\frac{p - p'}{p}$ and $\frac{p}{p'}$ are independent of temperature,

for heating the vapour in our bell-jar will change the pressures at the level 0 and at the level h in the same proportion. The relative lowering of vapour pressure should thus be independent of the temperature, if no molecular change in the nature of the vapour takes place.

These equations show that if solutions be prepared containing the same number of molecules of dissolved substance in the same number of molecules of solvent, the relative lowering of the vapour pressure will, on the assumptions specified, be equal in all cases. Thus if we have solutions in each of which there is one molecule dissolved in 100 molecules of solvent, the approximate equation gives

$$\frac{p-p'}{p} = \frac{1}{100} = 0{\cdot}010.$$

Raoult showed by experiment that if the same number of gram-molecules of various non-electrolytes were dissolved in water, or other solvent, the relative lowering of the vapour pressure was very nearly constant. He then took twelve solvents and, dissolving many bodies in each, proved that for a strength of solution of 1 molecule in 100 molecules the relative lowering of pressure was nearly constant, the mean value being about 0·0104.

In 1890, however, he found[1] that, when acetic acid was used as a solvent, the number obtained was 0·0163. This seems to differ from the results of our equations, but it must be remembered that in deducing them we assumed the molecular weight of the vapour to be the same as that which we took for the liquid. Now in reckoning the concentration of the solution the normal value of the molecular weight was taken for the liquid, and it is known that at moderate temperatures the vapour density of acetic acid is abnormal, showing that its molecular weight is also abnormal. At the boiling point, 118° C., the ratio of the actual to the normal vapour density is 1·64, which makes the value of n/N 0·0164. We must always correct the theoretical number in this way by mul-

[1] Raoult and Recoura, *Compt. Rend.* cx. p. 402, 1890.

tiplying it by the ratio of the actual to the normal vapour density.

Solutions of gases in liquids.

We have already seen (p. 84) that, with reference to their solubility in liquids, gases can be divided into two classes: firstly, those which are removed by boiling the liquid or decreasing the pressure, and secondly those which cannot be so removed.

In the first case, where the dissolved gas obeys Henry's law that the mass dissolved is proportional to the pressure, the laws of the vapour pressure are very simple. Let us consider a mass of air saturated with water vapour over a saturated solution of air in water. We know that if the external pressure be reduced, some air will at once come out of solution, while if the pressure be increased more goes in. If we have then some water with air dissolved in it over the mercury in a barometer tube, air will be expelled till that present in the barometric vacuum is in equilibrium with that dissolved, and whatever changes may occur in order that there may be equilibrium, the water must always keep saturated with air under the existing conditions of temperature and pressure. The pressure of aqueous vapour from the solution will obey the usual laws, and will therefore be less than that from pure water in accordance with our approximate equation

$$\frac{p-p'}{p} = \frac{n}{N},$$

or

$$p' = p\left(1 - \frac{n}{N}\right),$$

for the air in solution will exert osmotic pressure just like other substances. The total vapour pressure of the solution will be the sum of this and of the pressure due to the air, which, as we have seen, equals that in the vacuous space. This latter will depend on the relative volume of the solution and of the vacuous space, which takes air from the solution till there is equilibrium, so the measured vapour pressure would depend on the dimensions of the apparatus. We can however calculate the total vapour pressure in any given case if we know the final

concentration of the solution. Thus if there are n gram-molecules of gas dissolved in N gram-molecules of solvent, the diminution of the pressure of aqueous vapour (due to osmotic pressure) is for dilute solutions

$$p - p' = p\frac{n}{N}.$$

If we know λ_0, the solubility of the gas at the standard atmospheric pressure and 0° C., we can find the vapour pressure of the dissolved gas, for

$$\lambda_0 = \frac{v_0}{V},$$

where v_0 is the volume of gas dissolved under normal conditions and V the volume of the solution.

In a volume v_0 c.c. there are $v_0/22320$ gram-molecules. Let us call this number n_0, then by Henry's law

$$\frac{n}{n_0} = \frac{p}{A},$$

where p is the pressure of gas.

Therefore $$p = A\frac{n}{n_0} = \frac{A \times 22320\, n}{\lambda_0 V}.$$

V, the volume of the solvent, contains $\frac{V\rho}{M}$ gram-molecules, where M = molecular weight and ρ the density of the solvent.

Hence $$V = \frac{MN}{\rho},$$

and $$p = \frac{A \times 22320\, \rho}{\lambda_0 M}\frac{n}{N}.$$

This gives the increase in the total vapour pressure due to the gaseous pressure, so the total increase in the vapour pressure is

$$\left(\frac{A \times 22320\, \rho}{\lambda_0 M} - p\right)\frac{n}{N}.$$

In the second case of gases dissolved in liquids we have a solution like that of hydrochloric acid gas, which on distillation grows either richer or poorer in HCl till a certain concentration is reached. The solution then distils over

unchanged. This is exactly analogous to the solution of one volatile liquid in another and has already been considered qualitatively on p. 75.

Experimental measurements of vapour pressures.

Determinations of the vapour pressures of solutions have been made by Faraday, Wüllner, Tammann, Emden, Raoult, Walker, Beckmann, and others. Raoult[1] was the first to examine solutions of organic substances, and to use solvents other than water. His method consisted in comparing the heights of three mercurial barometric columns, the space over one being empty, and the others containing the vapours from the pure solvent and from the solution respectively. The depressions of these columns as compared with the first gave the vapour pressure of the solvent and of the solution. Raoult found that

(i) The relative lowering of the vapour pressure

$$(p - p')/p$$

is independent of temperature.

(ii) For dilute solutions $(p - p')/p$ is proportional to the concentration n/N, but as the solutions get stronger it is more nearly represented by $n/(N + n)$, where n and N are the numbers of molecules of dissolved substance and of solvent respectively.

(iii) The molecular lowering of vapour pressure (i.e. the lowering produced by 1 gram-molecule in 100 grams of solvent) is independent of the nature of the dissolved substance. Thus for ethereal solutions he found

	Molecular weight	Molecular lowering
Carbon hexachloride	237	·71
Turpentine	136	·71
Cyanic acid	43	·70
Benzaldehyde	106	·72
Aniline	43	·71
Antimony chloride	228·5	·67

(iv) When the ratio of the number of molecules of the dissolved substance to the number of molecules of the solvent

[1] *Compt. Rend.* CIII. p. 1125, 1886–7; CIV. p. 1430.

is made the same, the relative lowering of vapour pressure is independent of the nature of the substance and of the solvent, and is measured by the value of $\frac{n}{N+n}$.

This is shown by the following experimental results:

Solvent	Temperature in degrees Centigrade	$\frac{n}{N+n}$ (corrected for vapour density)	$\frac{p-p'}{p}$ (observed)
Water	100	0·0102	0·0102
Ethyl alcohol	78	0·0101	0·0101
Ether	20	0·0103	0·0104
Carbon bisulphide	24	0·0100	0·0099
Benzene	80	0·0101	0·0101
Acetic acid	118	0·0162	0·0163

We have already deduced all these results from the known values of the osmotic pressures, $\frac{n}{N+n}$ being practically the same as n/N for dilute solutions.

There are several objections to the barometric method. The quantity of vapour is so small that any impurity more volatile than the liquid would produce a large error, and since evaporation only occurs at the surface, the upper layers of the solution become stronger, and give too small a vapour pressure. Beckmann[1] improved the method by allowing the solution to evaporate into a small flask. He then calculated the quantity of vapour produced from the decrease in weight of the solution, which was contained in a weighed bulb.

A method applicable to low temperatures has been introduced by Ostwald and Walker[2]. A current of air is passed through two bulbs containing the solution, and is thus saturated with its vapour. It is then led through another bulb containing pure water. Since this gives a higher vapour pressure, the air takes up more water and again becomes saturated. Finally the whole of the aqueous vapour is extracted by passing the air

[1] *Zeits. phys. Chem.* IV. 532 (1889).
[2] *Zeits. phys. Chem.* II. 602 (1888).

through pumice moistened with sulphuric acid. The gain in weight of the sulphuric acid gives the whole quantity of vapour evaporated, and the loss in weight of the water bulb gives the difference between the quantity furnished by it and that furnished by the solution. Thus the ratio $(p-p')/p$ is at once found.

Tammann[1] has measured vapour pressures at 100° by noticing what decrease of external pressure was required to make the liquid boil at that temperature. He gives an immense number of figures showing the diminution of vapour pressure in millimetres of mercury, due to the solution of n gram-molecules in 1000 grams of water. We select a few of his results to which we shall have occasion to refer.

	$n=0{\cdot}5$	1	2	3	4	5	6
Potassium chloride	12·2	24·4	48·8	74·1	100·9	128·5	152·2
Sodium „	12·3	25·2	52·1	80·0	111·0	143·0	176·5
Potash (KOH)	15·0	29·5	64·0	99·2	140·0	181·8	223·0
Aluminium chloride	22·5	61·0	179·0	318·0			
Calcium „	17·0	39·8	95·3	166·6	241·5	319·5	
Barium „	16·4	36·7	77·6				
Succinic acid	6·2	12·4	24·8	36·7	48·5	59·7	71·2
Citric „	7·9	15·0	31·8	50·0	71·1	92·8	
Lactic „	6·5	12·4	24·0	34·3	44·7	55·0	65·6

If we calculate the theoretical depression for a concentration of 0·5 gram-molecule in 1000 grams of water from equation (24) on p. 128

$$\frac{p-p'}{p}=\frac{n}{N},$$

we get $p-p'=760\times\dfrac{0{\cdot}5}{\frac{1000}{18}}=6{\cdot}8$ mm. of mercury.

Thus we see that bodies like lactic and succinic acids give a result which agrees well with theory, while metallic salts are abnormal. Salts like potassium chloride, KCl, give numbers nearly double the figure deduced from theory, calcium and barium chlorides, $CaCl_2$ and $BaCl_2$, produce nearly three times, and aluminium chloride, $AlCl_3$, nearly four times the normal effect.

[1] *Mém. Acad. Pétersb.* xxxv. No. 9, 1887. Table in Ostwald's *Lehrbuch.*

As we have seen in considering osmotic pressure, these exceptions to the usual law all occur in the case of electrolytes. It is also important to note that KCl contains two atoms, $CaCl_2$ three atoms and $AlCl_3$ four atoms. The lowering of the vapour pressure by electrolytes seems then to be proportional to the number of atoms in the molecule. The discussion of these relations must be postponed for the present.

Tammann's results show that in general the lowering of vapour pressure increases faster than the concentration for metallic salts, but appears to be nearly proportional to it for indifferent substances. The concentration of Tammann's solutions is expressed in terms of the number of gram-molecular weights of salt dissolved in 1000 grams of water. If we convert this into the number of gram-molecules in 1000 grams of solution, the molecular lowering of vapour pressure will increase faster than Tammann's numbers do as the concentration gets greater.

Boiling points.

It is more convenient in some cases to measure the boiling point of a solution than its vapour pressure at any other temperature. Since the effect of the dissolved substance is to reduce the vapour pressure at any given temperature, it must raise the boiling point, and the relation between the two is easily found. Let ΠΠ in Fig. 41 be a portion of the vapour pressure curve of a solvent and Π′Π′ a portion of that of a solution. If the solution is dilute, so that the change in the vapour pressure is small, we may consider the part of the curve for the pure solvent that we want to use to be a straight line. Any vertical line cutting ΠΠ in A and Π′Π′ in B will represent the change in vapour pressure at the corresponding temperature, and CB drawn horizontally from the point B to cut ΠΠ in C, will represent the change in boiling point, δT.

Now whatever be the direction and form of the solution curve Π′Π′,

$$AB = CB \tan ACB.$$

Thus

$$p - p' = \delta T \tan ACB$$

$$= \delta T \cdot \frac{dp}{dT} \quad \ldots\ldots\ldots\ldots\ldots\ldots (26).$$

If we observe δT and know dp/dT for the pure solvent, we can at once calculate $p - p'$. The value of dp/dT can be experimentally determined by measuring the boiling point of the solvent first when the barometer is high and then when it is low, and dividing the difference in pressure by the difference in temperature.

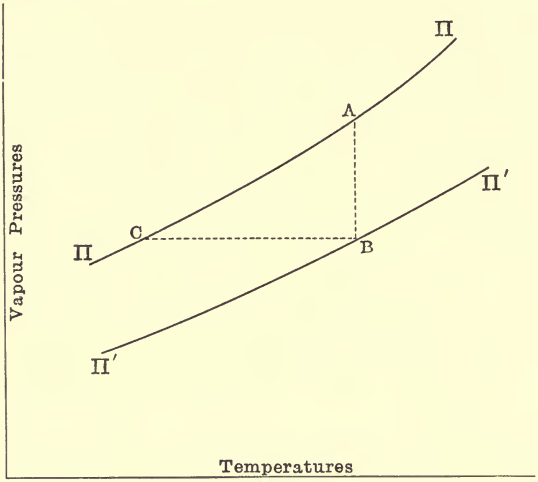


Fig. 41.

Another method of getting dp/dT is to use the latent heat equation

$$\frac{dp}{dT} = \frac{\lambda}{(v_2 - v_1)\,T},$$

where λ = latent heat, v_2 the volume of the saturated vapour and v_1 the volume of the liquid. If we assume that the vapour obeys the gaseous law $pv = RT$, we get, since v_1 is small,

$$\frac{dp}{dT} = \frac{\lambda p}{RT^2},$$

therefore

$$p - p' = \delta T \frac{\lambda p}{RT^2}$$

or

$$\frac{p - p'}{p} = \delta T \frac{\lambda}{RT^2} \quad \text{.....(27).}$$

Now we will assume that for 1 gram-molecule of the vapour the value of R is 1·980 calories: calling this 2, we can put

$$\frac{p - p'}{p} = \delta T \frac{\lambda}{2T^2} \quad \text{.....(28).}$$

From this expression the relative lowering of vapour pressure can be calculated from observations on the rise of boiling point.

In order to examine the validity of our theory, let us calculate δT for a special case. Assuming that the law of proportionality holds at such concentrations, the equation on p. 129 shows that, for a strength of solution of 1 molecule in 100 molecules of solvent, $(p-p')/p$ is equal to ·01; so for this concentration our equation gives

$$\delta T = \frac{\cdot 02 T^2}{\lambda} \quad \ldots\ldots\ldots\ldots\ldots\ldots (29).$$

The boiling point method was placed on a satisfactory footing by Beckmann[1], whose apparatus in some form is now usually employed. It is necessary to measure the temperature of the solution, and not the temperature of its vapour which, although it comes off at the boiling point of the solution, soon cools to its saturation temperature; condensation then begins and keeps the temperature of the vapour constant and equal to the condensing or boiling point of the pure solvent. To prevent "bumping" a piece of platinum wire is sealed through the bottom of the flask. Boiling then takes place exclusively from the end of this, and a constant and uniform stream of bubbles is given off. The following table gives the calculated values of $\cdot 02 T^2/\lambda$, and the mean results for the molecular rise of boiling point, deduced from observations on very dilute solutions in different solvents by means of Beckmann's apparatus.

Solvent	δT (observed)	$\frac{\cdot 02\, T^2}{\lambda}$ (calculated)
Water	4 to 5	5·2
Alcohol	10 to 12	11·5
Acetone	17 to 18	16·7
Ether	21 to 22	21·1
Carbon bisulphide	22 to 24	23·7
Acetic acid	25	25·3
Ethyl acetate	25 to 26	26·0
Benzene	25 to 27	26·7
Chloroform	35 to 36	36·6

[1] *Zeits. phys. Chem.* IV. 539 (1889).

The problem of accurately determining the boiling point of a solution is different from that which arises when the boiling point of a pure liquid is required. Regnault's method of measuring the latter is described in most text-books of physics. It consisted in immersing as much of the stem of the thermometer as possible in a current of vapour from the boiling liquid, the vapour being contained in a copper cylinder the outside of which was also surrounded by a jacket of vapour. The thermometer passed through a cork and the top of the mercury column projected above in order that it might be visible. The uncertainty of temperature in this part of the stem causes an error both in graduating a thermometer and in determining boiling points. It has also been shown by J. Y. Buchanan[1] that the jacket of vapour is unnecessary, the latent heat of the vapour keeping the inside of the vapour chamber, on which a film of liquid forms, accurately at the boiling point. It is therefore better to boil the liquid in a flask and to pass the vapour through a vertical glass cylinder about 4 centimetres in diameter which is narrowed below and fitted into the flask, the vapour escaping above directly into the air by a horizontal outlet. The thermometer can then be wholly immersed in the vapour, and read through the transparent walls of the cylinder. Even if involatile impurities are present in the liquid, the vapour which comes off is pure, and pure liquid will therefore condense on the bulb of the thermometer until its temperature is such that there is equilibrium between the film of pure liquid and its vapour. The thermometer must therefore show the boiling point of the pure liquid.

Now let us pass to the consideration of the case of solutions. If a current of steam be passed into an aqueous solution of a salt, condensation occurs until the temperature rises beyond the temperature of the steam and reaches the boiling point of the solution. The explanation of this remarkable fact is seen if we remember that the boiling point of a solution is the temperature at which it is in equilibrium with the vapour arising from it. At lower temperatures, therefore, vapour will condense on the

[1] *Trans. R. S. E.* xxxix. 547 (1899); also *Chemical and Physical Notes*, 1901.

surface of the solution, and its latent heat, which is of course really molecular energy transformed into heat, warms the liquid and vapour till the boiling point is reached. Thus a current of vapour passed through a solution must come out at the temperature of the boiling solution, and the same statement will hold good for the steam generated by the boiling of the solution itself: the steam from a boiling solution must come off at the boiling point of the solution. This, at first sight, appears contrary to the fact that a thermometer in the vapour registers the boiling point of the pure solvent, but, as soon as the vapour emerges from the solution, it is cooled by contact with the walls of the vessel, etc., and will therefore fall in temperature until the point of equilibrium with the pure solvent is reached The steam is then saturated, and the slightest further cooling will cause condensation on the walls or on an immersed thermometer. The latent heat set free by this condensation will warm the system and prevent it falling below the boiling point of the pure solvent. Thus the walls of the steam chamber and any thermometer hung in it will be constantly maintained at the temperature of the boiling point of the pure solvent, and, in order to determine the boiling point of a solution, the thermometer must be placed in the liquid itself.

The passage of steam through a solution has been applied by Buchanan in a convenient method of measuring the boiling points of saturated solutions, or, when these temperatures are known, of checking the graduations of a thermometer at parts of its scale above the boiling point of water. A quantity of dry salt in small crystals is placed in the glass cylinder shown in Fig. 42, and a current of steam is then passed through, till in a few minutes, a mixture of boiling saturated brine and salt is produced, which remains at a constant temperature until nearly all the salt is dissolved.

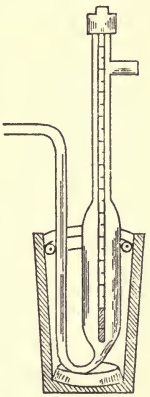


Fig. 42.

The boiling point of a solution, like that of a pure liquid, depends on the barometric pressure to which it is

subject. The change of boiling point for a given change of pressure is not the same for a solution as for its pure solvent, but the considerations detailed at the beginning of this chapter show that the ratio of the vapour pressures of solution and solvent, or the relative lowering of vapour pressure of a solvent produced by dissolving in it some solute, is constant at any temperature.

A promising way of measuring the boiling points of non-saturated solutions has been described by E. B. H. Wade[1]. The essence of the method consists in determining the difference in temperature between a solution and its solvent, boiling in similar vessels under the same atmospheric or artificial pressure. A difference in temperature can be easily and accurately measured by means of two platinum thermometers consisting of two equal coils of platinum wire wound on mica frames at the bottom of two long glass tubes. The difference between the electrical resistances of these coils gives at once the difference in temperature between them. Such duplicate measurements are free from errors due to changes in the pressure, which affect the results when the boiling points of solvent and solution are observed on different occasions. The liquids were heated by passing currents of steam through them, and at the instant when the measurement was made, solution was withdrawn for analysis.

Determination of molecular weights.

Like the depression of the freezing point, the lowering of vapour pressure has been used to determine the molecular weight of bodies in solution. It can be used for high temperatures, and for cases, such as for solutions in alcohol, when the freezing point method is not applicable. In this way Beckmann obtained the molecular weights of iodine, phosphorus and sulphur in solution. It was found that 1·065 grams of iodine, dissolved in 30·14 grams of ether, raised the boiling point by 0·296°. This concentration corresponds to $(1{\cdot}065 \times 7400)/(30{\cdot}14 \times M)$ gram-molecules of iodine in 7400 grams (100 gram-molecules) of ether. Now it can be proved either by experimenting with

[1] *Proc. R. S.* LXI. 285, 1897 and LXII. 376, 1898.

a body of known molecular weight, or by calculation from our formulae, that 1 gram-molecule of any non-electrolyte, dissolved in 100 gram-molecules of ether, gives a change in the boiling point of 0·284°. The above strength of solution must therefore be 296/284 gram-molecules.

Therefore $$\frac{1{\cdot}065 \times 7400}{30{\cdot}14\,M} = \frac{296}{284},$$

so that $$M = 250{\cdot}3.$$

The atomic weight of iodine is 127, so that in ethereal solution the molecule consists of two atoms.

In a similar manner it was shown that the molecule of phosphorus in carbon bisulphide contains 4 atoms, as it also does in the state of vapour, but that in the same solvent the molecule of sulphur consists of 8 atoms, whereas the vapour density gives a formula S_8.

The vapour pressures of amalgams have been examined by Ramsay[1], who found that in nearly all cases the lowering of vapour pressure corresponded to that which would be produced by monatomic molecules. The value deduced for the molecular weight of potassium is however less than its atomic weight (29·6 instead of 39·1) and the numbers for calcium and barium (19·1 and 75·7) correspond to half their atomic weights. What this means it is as yet impossible to say. Aluminium and antimony tend to form more complex molecules.

Freezing points.

It is obvious from what has been said in Chapter II that the true freezing point of a substance is the temperature at which the three phases, solid, liquid, and vapour, are in equilibrium with each other, giving a non-variant system. In other words, it is the temperature at which solid and liquid are in equilibrium under the natural pressure of the vapour. As commonly understood, however, the pressure under which the equilibrium exists is not that of the vapour corresponding to the temperature of the freezing point, but that of the atmosphere. Thus, in the case of water, the saturation pressure of the vapour at the freezing point is about

[1] *Chem. Soc. Journ.* p. 521, 1889.

4·7 mm. of mercury, and the true freezing point is, as we have seen, about 0°·007 higher than the temperature of equilibrium under the atmospheric pressure of 760 mm.

Since the change in volume on fusion is usually small, the latent heat equation shows that the change of freezing point with pressure is small also, and there is usually not much difference between the two freezing points. We shall, therefore, for the sake of convenience, understand the freezing point to be determined under atmospheric pressure, remembering that, to deduce from it the true transition point of the substance, the pressure correction must be applied.

The freezing point of a solution, as we have seen, is in general different from that of its pure solvent, the direction of the change depending on the nature of the solid which freezes out. When the solid separating is that of the pure solvent, the freezing point of the solution is always lower than that of the solvent, and for dilute solutions the depression is related to the osmotic pressure by equation (22) on p. 126

$$\delta\theta = \frac{P\theta}{\lambda\rho}.$$

If the solid is not the pure component, a study of the freezing point curve will generally, as we have seen in Chapter III, enable a knowledge of the nature of the solid to be deduced. In the case of salt solutions, the ice is usually that of pure water, and a proof of this fact has been given for solutions of sodium chloride by J. Y. Buchanan[1]. The ice as it freezes out always entangles some brine among its crystals, and this salt is so difficult to remove that it has often been thought to form an integral part of the solid phase. Buchanan showed, however, that the impure ice so obtained, when immersed in a salt solution, reduced it to exactly the same temperature as pure ice reduced a solution of the same final concentration, allowing, that is, for the salt added to the solution by the impure ice.

The phenomena of the cryohydric point have already been considered in the light of the phase rule, which regards it as the non-variant point at which the system is completely

[1] *Proc. R. S. E.* xiv. 129; also *Nature*, xxxv. 516 and 608, xxxvi. 9, 1887.

determined, and a transition from liquid to solid or *vice versâ* occurs without change of temperature. The subject must now be further considered, and some applications of the principles deduced made to the phenomena of freezing. Experimental determinations of cryohydric temperatures for many different salts have been made, among others by L. C. de Coppet[1], from whose results we take the numbers which follow.

Salt		Cryohydric temperature in Centigrade degrees	Weight of anhydrous salt in 100 parts of water
Potassium chloride	KCl	−11·1	24·6
Sodium chloride	$NaCl$	−21·85	29·6
Ammonium chloride	NH_4Cl	−15·8	22·9
Strontium chloride	$SrCl_2$	−18·7	—
Barium chloride	$BaCl_2.2H_2O$	− 7·85	25·1
Zinc sulphate	$ZnSO_4.7H_2O$	− 6·55	37·3
Copper sulphate	$CuSO_45H_2O$	− 1·6	13·5
Ammonium sulphate	$(NH_4)_2SO_4$	−19·05	62·2
Potassium chromate	K_2CrO_4	−11·3	57·7
Sodium sulphate	$Na_2SO_4.10H_2O$	− 1·2	4·0
„ „	$Na_2SO_4.7H_2O$	− 3·55	14·5
Sodium carbonate	$Na_2CO_3.10H_2O$	− 2·1	5·3
Potassium nitrate	KNO_3	− 2·85	10·7
Sodium nitrate	$NaNO_3$	−18·5	58·5
Ammonium nitrate	NH_4NO_3	−17·35	70·0
Barium nitrate	$Ba(NO_3)_2$	− 0·7	4·5
Strontium nitrate	$Sr(NO_3)_2$	− 5·75	32·4
Lead nitrate	$Pb(NO_3)_2$	− 2·7	35·2

If a solution be continually cooled ice will separate, and, since it is the ice of pure water, the residual solution becomes more and more concentrated, and its freezing point, therefore, lower and lower, till the cryohydric point is reached. Any further cooling will then deposit salt side by side with the ice, and the composition of the liquid phase remains constant as long as any liquid is left. At certain stages in the process, therefore, there will be crystals of ice separated by mother-liquid, the composition of which is that of the cryohydric mixture. The sizes of these crystals will depend on the nature of the freezing operation, its speed and the amount of stirring to which the liquid was subject during the process. Even the purest natural water contains a certain quantity of dissolved

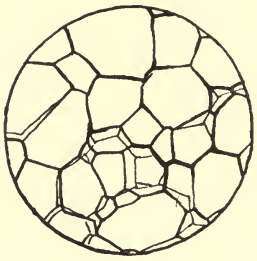
[1] *Zeits. phys. Chem.* XXII. 239 (1897).

matter, and thus natural ice has always a grained structure, the crystalline elements being separated by a film of liquid brine, the thickness of which depends on the amount of impurity originally present in the water. Only when the temperature is below the cryohydric point does the whole mass become solid, the cryohydrate acting as a kind of cement connecting the grains of pure ice. The dissolved air, which is always present to some extent in natural water, greatly increases the granular appearance of the structure. As the ice forms, this air is gradually expelled from solution; but the last traces of it, remaining in the films of liquid cryohydrate, are entangled as bubbles when the films solidify and thus further emphasize the lines of separation between the primary crystals. The grained structure is well seen if a block of natural ice, taken, say, from the inside of a glacier, is exposed to the sun's rays. The block is rapidly disintegrated, and is finally reduced to a heap of crystalline grains.

The corresponding structure has been observed for mixtures

Gold aluminium alloy.
Magnification 450.

Fig. 43.



Cadmium.
Magnification 100.

Fig. 44.

of metals. Microscopic photographs of alloys show clearly the crystals of the first solid formed (sometimes a pure component and sometimes a metallic compound) separated by channels of eutectic alloy which has solidified at a lower temperature than the crystals imbedded in it. Fig. 43[1] is drawn from one of

[1] *Phil. Trans.* A. CXCIV. 201, Plate 4 (1900).

Heycock and Neville's photographs of an alloy of gold and aluminium containing 19·8 atomic per cents. of aluminium. Fig. 44, in like manner, shows a photograph by Ewing and Rosenhain[1] of a surface of cadmium cast on a glass plate. The thinness of the connecting lines here indicates that the metal is very nearly pure. The slight traces of other metals present, as well as any gases dissolved in the molten metal, are concentrated in the channels left between the crystals as they slowly cool.

Returning to the case of water, we observe that, as Buchanan has pointed out, the power which ice in the form of a glacier possesses of flowing along a curved bed may be partly due to these channels of low-freezing liquid between the solid grains. The liquid films allow the ice to yield slightly under stress, and then the heat developed by the grinding of the crystals over each other raises the whole mass to the freezing point of pure water, and enables the regelation of ice (i.e. the melting of the solid under high pressure and its freezing again when that pressure is removed) to come into play and help the flow, in the manner suggested by the usual explanation of the plasticity of ice. The fracture of solid crystals and the sliding of the broken parts over each other under the action of a shearing stress has been described in the case of metals by Ewing and Rosenhain.

The phenomena of the freezing of sea water under the influence of the intense cold of an arctic climate is an interesting example of the application of these principles. The process has been described by the explorer Weyprecht[2], whose account is quoted by Buchanan. When a new surface of sea water is exposed to the cold air, in a short time the surface of the water begins to get thick, threads like a spider's web running out from the old ice. Brine is entangled in this structure, and its concentration continually gets greater as the quantity of ice increases. At this stage the ice is a pasty mass and follows every motion of the water on which it floats. With a tem-

[1] *Phil. Trans.* A. CXCIII. 353, Plate 26 (1899).

[2] *Die Metamorphosen des Polareises*, Wien (1879).

perature of $-40°$ C. the new ice, even after twelve hours, is still so soft that, in spite of its thickness, a stick can easily be thrust through it.

As soon as a layer of ice is formed over the surface, the cooling of the underlying water proceeds much more slowly, and less salt is entangled in the crystals. The lower layers of sea water ice therefore give, when melted, a much fresher water than can be obtained from the upper layers. Even when strong enough to walk on, the surface of new sea water ice frozen by air at $-40°$ C. is still moist and soft, the residual liquid consisting of a concentrated solution of various salts, chiefly calcium chloride. The cryohydric point of calcium chloride, a very soluble substance, is very low, and that of a mixture of salts, unless they form mixed crystals, will be lower than that of either component, just as is the freezing point of a mixture of metals. This lowering of the cryohydric temperature was observed by Buchanan in experiments conducted in the Engadine.

It is obvious that the cryohydric mixture can be prepared by cooling a solution of any concentration and letting it freeze till the temperature becomes constant; the liquid remaining, if it be poured off, will freeze throughout at a constant temperature, and then give the cryohydrate. Another method of preparation consists in mixing intimately snow or finely powdered ice with the powdered solid. Salt dissolves and melts some of the ice, the latent heat of which causes the temperature to fall until the cryohydric point is reached, when a saturated solution of the salt at its freezing point is in equilibrium with ice. It is evident, then, that ice and salt together form what is called a freezing mixture. In order to get the full cooling effect, the finely divided ice or snow should be dry, that is, well below the freezing point of water, otherwise the adherent moisture will soon be frozen when the mixture is made, and further contact between the parts prevented. The salt, too, should be cooled below 0° before mixture. The temperature will sink more rapidly, also, if a salt be used which dissolves with an absorption of heat, for then this cooling effect is added to the other.

From equation (22) for indefinitely dilute solutions, deduced on p. 126, namely

$$\delta T = \frac{PT}{\lambda\rho},$$

it is easy to calculate numerically the lowering of the freezing point of a solvent produced by dissolving in it a small quantity of some non-electrolyte.

Let us take the case of a water solution of any body containing one gram-molecule per litre. We have seen (pp. 104, 120) that the osmotic pressure is the same as the dissolved molecules would exert in the gaseous state. It is therefore 22·32 atmospheres, or $22{\cdot}32 \times 76 \times 13{\cdot}6 \times 981$ C.G.S. units.

For water $\rho = 1$, $T = 273$ and $\lambda = 79{\cdot}4$ calories or

$$79{\cdot}4 \times 4{\cdot}184 \times 10^7 \text{ ergs.}$$

If we calculate δT with these numbers we find that the freezing point of water should be lowered by one gram-molecule of dissolved substance per litre, by

$$1°{\cdot}857 \text{ C.}$$

Raoult[1] made many experiments on this subject and his results give a mean value of

$$1°{\cdot}85 \text{ C.}$$

for the same effect. Other observers have subsequently found results for cane-sugar differing considerably from this value; but just lately E. H. Griffiths, using the most exact methods of platinum thermometry, has found that for dilute solutions of cane-sugar in water, ranging in strength from 0·0005 normal to 0·02 normal, the molecular lowering of freezing point is

$$1{\cdot}858.$$

It is easier to make a comparison with Raoult's results by changing the form of our equation, but the effects of dissolved bodies on any solvent can be calculated from (22) by using the values for T and λ given on p. 149. This equation is the simplest expression of Van 't Hoff's theory, and the one which shows most clearly the connexion between the lowering of freezing

[1] *Comp. Rend.* XCIV. p. 1517 (1882).

point and the osmotic pressure; another form however may be useful.

In our equation (22) let us put, since dilute solutions obey Boyle's law,

$$Pv = RT,$$

v being the volume of solution containing one gram-molecule of solute. The expression then becomes

$$\delta T = \frac{RT^2}{\lambda v \rho} \quad \text{.....(30).}$$

R is a constant of which the value for one gram-molecule of any gas or substance in dilute solution is, as we have shown on p. 4,

$$R = \frac{pv}{T} = 8{\cdot}284 \times 10^7 \text{ ergs per degree}$$
$$= 1{\cdot}980 \text{ calories per degree,}$$

taking as the most probable value for the mechanical equivalent of heat $4{\cdot}184 \times 10^7$.

Now $$v = \frac{1000}{n},$$

where n represents the number of gram-molecules per litre. We then get

$$\delta T = \frac{1{\cdot}980\, T^2}{1000 \lambda \rho}$$
$$= \frac{0{\cdot}001980\, T^2 n}{\lambda \rho} \quad \text{.....(31).}$$

In the case of water this gives $\delta T = 1{\cdot}86° n$, and of course the value for other solvents can be deduced in a similar manner.

Raoult expressed the concentrations of his solutions in terms of the number of gram-molecular weights of substance dissolved in 100 grams of the solvent. From observations on more dilute solutions, he calculated, on the assumption that the law of proportionality was still applicable, the depression of the freezing point which would be produced by one gram-molecule dissolved in 100 grams of solvent.

We can at once throw our equation (22) into a form in which comparison with Raoult's results for different solvents is easy. The volume of 100 grams of solvent is $\frac{100}{\rho}$. We have

seen that for dilute solutions, the osmotic pressure has the gaseous value 22·3 atmospheres per gram-molecule per litre. For such solutions, the density of the solution is the same as that of the solvent, and, if the law of proportionality still held good, when we dissolve one gram-molecule in $\frac{100}{\rho}$ c.c., we should get a pressure which is greater than that given by one gram-molecule per litre in the ratio of

$$1000 : \frac{100}{\rho} \text{ or } 10\rho : 1.$$

The value of n becomes 10ρ times greater than before and equation (31) assumes the form

$$\delta T = \frac{0{\cdot}00198\, T^2}{\lambda\rho} \times 10\rho = \frac{1{\cdot}98\, T^2}{100\,\lambda} = \frac{2T^2}{100\,\lambda} \quad \ldots\ldots(32).$$

The comparison between the values calculated from this equation by Van 't Hoff, and Raoult's observed numbers is given below.

	T	λ	$\frac{2T^2}{100\lambda}$	δT (observed)
Water	273°	79·4	18·57	18·5
Acetic acid	290	43·2	38·8	38·6
Formic acid	281·5	55·6	28·4	27·7
Benzene	277·9	29·1	53·0	50·0
Nitrobenzene	278·3	22·3	69·5	70·7

The agreement between these results is sufficient to show that, at all events in dilute solutions, the theory of Van 't Hoff, according to which the osmotic pressure has the same absolute value as gaseous pressure, leads to results which agree with observation to a considerable degree of accuracy.

Raoult stated that one molecule of a substance dissolved in 100 molecules of solvent always gave a depression of the freezing point which was approximately equal to 0·63, and supported this generalization by experiments on solutions in formic acid, acetic acid and benzene. Theory gives no ground for such an assertion, but if we work out formula (32) for these particular

cases, we shall find that, as a matter of fact, the numbers all happen to be nearly what Raoult gave. If the molecular weight of the solvent be M, the quantity represented by 100 gram-molecules is M times that represented by 100 grams, so that the solutions will be only $1/M$ as strong as those we dealt with in the last table. The depression of the freezing point will therefore be not $2T^2/100\lambda$, but $2T^2/100\lambda M$. If we divide the figures given in the table by the molecular weights of the solvents we get for the depressions

Formic acid = 0·62
Acetic acid = 0·65
Benzene = 0·68

The approximate constancy of these numbers is however a pure accident, and does not hold for other bodies; thus water gives 1·05. This point has been fully examined experimentally by Eykman[1], who concludes, although his result for naphthylamine seems to be abnormal, that the evidence is conclusive in favour of Van 't Hoff. In Raoult's original generalization he was misled by a purely accidental agreement of numbers, and he has since accepted Eykman's results and the accuracy of Van 't Hoff's formula.

Osmotic pressure and freezing point of concentrated solutions.

When the restriction limiting the treatment to the case of dilute solutions is removed, both the change of volume and the heat of dilution must be considered. This has been done by T. Ewan[2], from whose paper the following investigation has been adapted with simplifications. With the help of a semi-permeable membrane a reversible cycle can be performed.

Beginning with a mass of solution m, in equilibrium at its absolute freezing point T_1, with an indefinitely small quantity of ice, carry the system through the following cycle:

1. Allow dm gram of ice to freeze out, the heat which must be supplied to keep the temperature constant is

$$-L_1 dm + \frac{\partial Q_1}{\partial m} dm,$$

[1] *Zeits. f. physikal. Chemie*, III. 203, 1889.
[2] *Zeits. f. physikal. Chemie*, XXXI. 22, 1899.

where L_1 is the heat of fusion of one gram of ice and $\frac{\partial Q_1}{\partial m}$ the heat of dilution, both at the temperature T_1. The heat of dilution is measured at constant temperature and is therefore written as a partial differential.

2. Heat the ice and solution separately to T_0 the freezing point of the pure solvent on the absolute scale. The heat added is

$$dm \int_{T_1}^{T_0} C_i dT + (m - dm) \int_{T_1}^{T_0} \left(C_l - \frac{dC_l}{dm} dm \right) dT,$$

C_i being the specific heat of ice, and C_l that of the original solution.

3. Melt the ice at T_0. The heat added is $L_0 dm$, where L_0 is the heat of fusion of one gram of ice at T_0.

4. Return the water to the solution through a semi-permeable membrane at a constant temperature T_0. The heat supplied to maintain this constancy of temperature is

$$-\frac{\partial Q_0}{\partial m} dm + Pv dm,$$

where P is the osmotic pressure of the solution at T_0 and v is the increase in volume which the solution undergoes per gram of water added to it at constant temperature and concentration, the volume of the original solution being large.

5. Cool the solution thus formed to T_1. The heat added is

$$-m \int_{T_1}^{T_0} C_l dT.$$

All these operations are reversible, and at the end the system is exactly in its original condition. We can therefore apply the second law of thermodynamics and write

$$\int \frac{dQ}{T} = 0.$$

Collecting the terms and integrating we get (33)

$$\frac{L_0}{T_0} - \frac{L_1}{T_1} + \frac{1}{T_1} \frac{\partial Q_1}{\partial m} - \frac{1}{T_0} \frac{\partial Q_0}{\partial m} + C_i \log \frac{T_0}{T_1} - m \frac{dC_l}{dm} \log \frac{T_0}{T_1} + \frac{Pv}{T_0} = 0.$$

In order to reduce this to a form which involves only terms which can be experimentally determined we must notice:

(*a*) That a gram of ice at T_1 can be changed into a gram of water at T_0 by adding heat either

$$L_1 + C_w(T_0 - T_1) \text{ or } C_i(T_0 - T_1) + L_0.$$

Thus $$L_1 - L_0 = (C_w - C_i)(T_0 - T_1)$$

and $$\frac{L_1}{T_1} - \frac{L_0}{T_0} = L_0\left(\frac{1}{T_1} - \frac{1}{T_0}\right) + (C_w - C_i)\left(\frac{T_0 - T_1}{T_1}\right).$$

(*b*) The difference in heat-contents of the solution between T_1 and T_0 is

$$Q_0 - Q_1 = C_l m (T_0 - T_1).$$

Therefore $$\frac{\partial Q_0}{\partial m} - \frac{\partial Q_1}{\partial m} = m\frac{dC_l}{dm}(T_0 - T_1)$$

and $$\frac{1}{T_0}\frac{\partial Q_0}{\partial m} - \frac{1}{T_1}\frac{\partial Q_1}{\partial m} = \frac{\partial Q_0}{\partial m}\left(\frac{1}{T_0} - \frac{1}{T_1}\right) + m\frac{dC_l}{dm}\left(\frac{T_0 - T_1}{T_1}\right).$$

Substituting these values in equation (33) and expanding the logarithms

$$\begin{aligned}\frac{Pv}{T_0} &= L_0\left(\frac{1}{T_1} - \frac{1}{T_0}\right) + (C_w - C_i)\left(\frac{T_0 - T_1}{T_1}\right) + \frac{\partial Q_0}{\partial m}\left(\frac{1}{T_0} - \frac{1}{T_1}\right) \\ &\quad + m\frac{dC_l}{dm}\left(\frac{T_0 - T_1}{T_1}\right) + C_i\left\{\frac{T_0 - T_1}{T_1} - \frac{1}{2}\left(\frac{T_0 - T_1}{T_1}\right)^2 \cdots\right\} \\ &\quad - m\frac{dC_l}{dm}\left\{\frac{T_0 - T_1}{T_1} - \frac{1}{2}\left(\frac{T_0 - T_1}{T_1}\right)^2 \cdots\right\} \\ &= L_0\left(\frac{1}{T_1} - \frac{1}{T_0}\right) + C_w\left(\frac{T_0 - T_1}{T_1}\right) + \frac{\partial Q_0}{\partial m}\left(\frac{1}{T_0} - \frac{1}{T_1}\right) \\ &\quad - \frac{1}{2}C_i\left(\frac{T_0 - T_1}{T_1}\right)^2 + \frac{1}{2}m\frac{dC_l}{dm}\left(\frac{T_0 - T_1}{T_1}\right)^2.\end{aligned}$$

Thus $$\frac{P_v}{T_0} = \left(L_0 - \frac{\partial Q_0}{\partial m}\right)\left(\frac{1}{T_1} - \frac{1}{T_0}\right) + C_w\left(\frac{T_0 - T_1}{T_1}\right) - \frac{1}{2}\left(C_i - m\frac{dC_l}{dm}\right)\left(\frac{T_0 - T_1}{T_1}\right)^2 \quad \ldots\ldots\ldots\ldots (34),$$

an equation which gives the relation between the osmotic pressure and the depression of freezing point, $T_0 - T_1$.

Experiments on the freezing points of solutions.

It has long been known that the freezing point of a salt solution, such as sea water, is lower than that of the water when pure, and in 1788 Blagden[1] published some observations on the subject, which showed that the depression of the freezing point produced by dissolving a substance in water, was approximately proportional to the quantity of substance in solution, except when the concentration became considerable.

More recent observations were made by Rüdorff[2] and de Coppet[3]. The latter noticed that if the lowering of the freezing point produced by chemically equivalent quantities of different salts was examined, it was found that the molecular lowering was nearly equal for salts of similar chemical constitution.

The whole subject was first fully examined by Raoult[4], who extended his observations to non-electrolytes, such as solutions in pure benzene, and solutions of organic compounds in water. He found that the depressions produced by equi-molecular quantities of different substances were nearly of the same value.

Further measurements have been made by Arrhenius[5], H. C. Jones[6], Loomis[7], Wildermann[8], Archibald[9], Barnes[10], Pickering[11], and many others. The theory of such determinations has been treated by Nernst and Abegg[12], and since the publication of their results the precautions necessary to ascertain the true freezing point have been more fully understood.

[1] *Phil. Trans.*, LXXVIII. p. 277.

[2] *Pogg. Ann.*, 1861, 114 *et seq.*

[3] *Ann. Chim. Phys.*, 1871, II. 23, 25, 26.

[4] *Comp. Rend.* (1882), XCIV. p. 1517, XCV. pp. 188, 1030. *Ann. Chim. Phys.* (6), II. p. 66, (5), XXVIII. p. 137, (6), IV. p. 401. *Zeits. phys. Chem.* XXVIII. 617 (1898) and *Cryoscopie*, Paris 1901.

[5] *Zeits. phys. Chemie*, II. 491 (1888).

[6] *Zeits. phys. Chemie*, XI. 110 and 529 (1893); XII. 623 (1893).

[7] *Phys. Review*, I. 199 and 274 (1893–4); III. 270 (1896); IV. 273 (1897); XII. 220 (1901).

[8] *Zeits. phys. Chemie*, XIX. 233 (1896).

[9] *Trans. Nova Scotia Inst. Sci.* X. 33 (1898).

[10] *Trans. Nova Scotia Inst. Sci.* X. 139 (1899) and *Trans. R. S. Canada* [II.] VI. 37 (1900).

[11] *Chem. Soc. Jour.* 1893.

[12] *Zeits. für physikal. Chemie* (1894), XV. 7, 681.

The freezing point may, as we have said, be defined as the temperature at which an isolated mass of liquid can exist in permanent equilibrium with its own solid under the normal atmospheric pressure. It had been assumed that the stationary temperature assumed by a small quantity of a partly frozen liquid, contained in a vessel surrounded by a freezing mixture, gave at once the true freezing point, but Nernst and Abegg pointed out that this limited volume of liquid, radiating to an outer enclosure, would, irrespective of freezing, tend to reach a convergence or equilibrium temperature, which depends on the amount of heat evolved by stirring and on the temperature of the environment; and, unless this equilibrium temperature coincides with the freezing point, or unless the rate of approach to the freezing point is very great compared with the rate of approach to this temperature, the thermometer will not show the true freezing point.

The corrections necessary on this account can be experimentally determined, and Nernst and Abegg obtained good agreement between the results of experiments performed under conditions so different, that the uncorrected numbers for the molecular depression of the freezing point of a one per cent. solution of sugar varied from 1·6 to 2·1. Their mean corrected value is about 1·86—a number which agrees exactly with that calculated from the melting point and heat of fusion of ice (p. 147).

In order to make the convergence temperature coincide with the freezing point, Ponsot[1] formed crystals of ice in his solution by surrounding it with a freezing mixture, and then removed the vessel containing the solution, placing it in an air jacket which was surrounded by a vessel filled with a mixture of ice and brine of such a concentration that its temperature was as nearly as possible that of the solution to be examined. The solution is then in an enclosure at the temperature of its own freezing point, and the only variation in the convergence point is due to the heat evolved by stirring. When

[1] *Ann. de Chim. et de Phys.*, and *Congélation des Solutions Aqueuses*, Paris 1896.

the temperature becomes constant, therefore, it is very nearly indeed the true freezing point.

The apparatus generally used for freezing point determinations when great accuracy is not required was introduced by Beckmann, and is represented in Fig. 45.

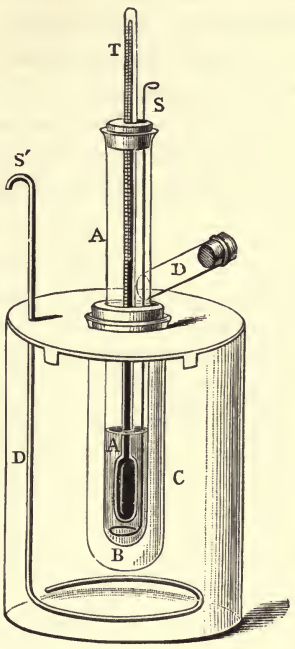


Fig. 45.

The solution to be examined is placed in a wide test-tube *A*, which is surrounded by a second larger tube *B* to serve as an air jacket. This is placed in a vessel *C*, into which a freezing mixture can be introduced. There is one stirrer in *C*, and another, made of a platinum wire, in *A*. A delicate thermometer graduated to hundredths of a degree, is also placed in *A*. It has a little reservoir at the top, into which some of the mercury can be driven, to make the instrument available for different solvents, which freeze at different temperatures.

The method of using Beckmann's apparatus is as follows. A weighed quantity of the pure solvent is introduced into *A*, and its freezing point determined by placing in *C* some mixture whose temperature is just below the point to be reached. The tube *A* is then removed, and the solvent melted. A weighed quantity of the substance to be dissolved is introduced through the side tube *D*, and the tube replaced. It is better to cool it slightly below the temperature at which it will finally stand. This can be done if it be kept quite at rest. The undercooled liquid is then stirred by means of the platinum wire, when small crystals of ice form. The temperature rises to a certain point, and then keeps stationary, but will again begin to sink if we go on freezing the solution; for as the solvent is frozen out, the remaining solution gets stronger, and so has a lower freezing point. The highest of these temperatures is

therefore the one giving the freezing point of the solution, the concentration being corrected for the volume of ice formed.

An immense number of observations have been made with one of the many forms of this apparatus. Some of Raoult's results are given below. They represent what he calls the molecular depression, that is the lowering which would be produced by one gram-molecule of the substance in 100 grams of the solvent. The numbers are calculated from observations on solutions of much less concentration than this, on the assumption that the law of proportionality is still applicable.

Solutions in Acetic Acid.

Van 't Hoff's formula gives 38·8.

Methyl iodide	38·8	Butyric acid	37·3
Chloroform	38·6	Benzoic „	43·0
Carbon disulphide	38·4	Water	33·0
Ethylene chloride	40·0	Methyl alcohol	35·7
Nitrobenzene	41·0	Ethyl „	36·4
Ether	39·4	Amyl „	39·4
Chloral	39·2	Glycerine	36·2
Formic acid	36·5	Phenol	36·2
Sulphur dioxide	38·5	Stannic chloride	41·3
Sulphuric acid	18·6	Magnesium acetate	18·2
Hydrochloric acid	17·2		

Solutions in Formic Acid.

Van 't Hoff's formula gives 28·4.

Chloroform	26·5	Potassium formate	28·9
Benzene	29·4	Arsenious chloride	26·6
Ether	28·2		
Aldehyde	26·1	Magnesium formate	13·9
Acetic acid	26·5		

Solutions in Benzene.

Van 't Hoff's formula gives 53·0.

Methyl iodide	50·4		
Chloroform	51·1	Methyl alcohol	25·3
Carbon disulphide	49·7	Ethyl „	28·2
Ethylene chloride	48·6	Amyl „	39·7
Nitrobenzene	48·0	Phenol	32·4
Ether	49·7	Formic acid	23·2
Chloral	50·3	Acetic „	25·3
Nitroglycerine	49·9	Benzoic „	25·4
Aniline	46·3		

Solutions in Nitrobenzene.

Van 't Hoff's formula gives 69·5.

Chloroform	69·9	Methyl alcohol	35·4
Benzene	70·6	Ethyl „	35·6
Ether	67·4	Acetic acid	36·1
Stannous chloride	71·4	Benzoic „	37·7

Solutions in Water.

Van 't Hoff's formula gives 18·9.

Methyl alcohol	17·3	Hydrochloric acid	39·1
Ethyl „	17·3	Nitric acid	35·8
Glycerine	17·1	Sulphuric acid	38·2
Cane sugar	18·5	Potash	35·3
Phenol	15·5	Soda	36·2
Formic acid	19·3	Potassium chloride	33·6
Acetic „	19·0	Sodium „	35·1
Butyric „	18·7	Calcium „	49·9
Oxalic „	22·9	Barium „	48·6
Ether	16·6	Potassium nitrate	30·8
Ammonia	19·9	Magnesium sulphate	19·2
Aniline	15·3	Copper „	18·0

An examination of these tables at once shows that the molecular depressions produced by different substances in the same solvent are approximately constant. Leaving out of consideration, for the present, solutions in water, we find that in other solvents, besides a series of normal compounds, having molecular depressions which agree with the number deduced from Van 't Hoff's theory, there is in general a series of abnormal substances which give depressions of about half this value. Since on Van 't Hoff's theory the effect is proportional to the number of dissolved molecules, and independent of their nature, it is at once suggested, that, in these cases, the number of molecules is halved owing to the formation of aggregates of two ordinary molecules, so that the molecular weight is doubled. There is further confirmation in that some of the compounds which show this effect (such for instance as the acids of the formic acid series, which give half values when dissolved in benzene or nitrobenzene) are known to form compound molecules in the gaseous state, and there is evidence from other sources (e.g. from the surface tensions) that these acids and also certain alcohols form polymeric molecules when liquid.

The most accurate experiments yet attempted on the freezing points of very dilute solutions are those of E. H. Griffiths, who has adapted the most refined methods of platinum thermometry to this problem. The details of the apparatus have not yet been published, but its general features together with the few final results which have already been obtained were described to the British Association in 1901. In order to avoid any action of the solutions on glass, the vessels containing them are of platinum and the water used is finally distilled from a platinum still. The duplicate principle of compensation is adopted, simultaneous observations being made on water and a solution, contained in similar platinum vessels. These vessels are completely surrounded, except for tubes of entrance for the thermometers, etc., by air jackets; the water apparatus is then immersed in a large bath of ice and water, and that holding the solution in a similar bath filled with ice and brine arranged to give, as nearly as possible, the anticipated temperature of the freezing point. The two sides are then frozen by evaporating ether in the air spaces; the local cooling produced by this operation soon disappears. Both the solution and the outer bath are kept constantly stirred by means of water motors, the heating effect due to the work thus done being the same on each side. Platinum thermometry is particularly sensitive when used in this differential manner, and about the hundred thousandth of a centigrade degree can be measured. A solution of cane sugar gave constant molecular depressions of the freezing point while the concentration was varied from 0·0005 to 0·02 normal, the numerical value of the molecular depression being 1°·858. A series of experiments on solutions of potassium chloride gave a limiting value of the molecular depression equal to 3°·720, which, on the assumption that KCl produces twice the effect of a single molecule, gives for the characteristic number, 1°·860, a result identical with that obtained for cane sugar within the limits of experimental error.

Determination of molecular weight.

It is evident then, that the determination of the freezing point of a solution affords a means of controlling the measurement of the molecular weight of

the dissolved substance. If we do not know whether the molecular weight of a body is M or nM, we can see which of these values we must use in calculating the molecular depression in order to get a number nearly equal to the theoretical value for the constant. It must be noticed that we only determine the molecular weight of a body in a certain solvent; for the same substance may have different molecular weights in different solvents (as witness the alcohols in benzene and acetic acid) and of course these values may be all different from its molecular weight in the gaseous state, though in general this weight corresponds to one of the others. The nature of the solvent may affect the state of molecular aggregation, even as it is affected by conditions of temperature and pressure when the substance is a gas. The solvents of the benzene series appear to favour polymerisation, while formic acid and its analogues seem generally to produce simple molecules.

In the case of aqueous solutions also we have two series, and, taken alone, we might be inclined to consider the higher numbers as normal, and to assign doubled molecular weights to those substances which give the lower values. But when we work out Van 't Hoff's formula for the case of water, it gives, as we have seen, a value 18·6 for the molecular depression. This at once shows that the lower numbers are the normal values, and that they can be explained on Van 't Hoff's theory. It is the higher series which requires some further explanation. Are we to suppose that, as in the case of certain gases at high temperatures, dissociation occurs, and increases the number of effective pressure-producing molecules, or are we to assume that some new cause is brought into operation? In favour of the dissociation hypothesis it may be urged that the numbers for such salts as KCl, NaCl, etc., which can only be dissociated into two parts, never show values which are much greater than double the normal, while salts such as $CaCl_2$, which can be split into three, sometimes give a molecular depression which is about three times the normal value. We must defer the fuller discussion of these phenomena till we are considering the electrical properties of solutions, but attention is here drawn to the important fact that all those substances which give

abnormally great values for the molecular depression of the freezing point in aqueous solution, form, when dissolved in water, solutions which are electrolytes. Moreover their electrical conductivities bear at all events an approximate relation to the amount of dissociation which it is necessary to assume in order to account for the abnormal effect on the freezing point. Whatever is the cause of this abnormally great molecular depression, seems to be also the cause of electrolytic conductivity.

Freezing points of alloys.

When metals are dissolved in mercury, they produce depression of the point of solidification, just as bodies dissolved in water produce depression of the freezing point. Tammann examined solutions of potassium, sodium, thallium and zinc, and found Raoult's laws approximately true. These metals seem to form monatomic molecules.

Heycock and Neville[1] have used many metals as solvents, and found values for the atomic depressions of which we select the following:

Solutions in Tin. Theoretical depression, 3°·0.

Silver	2·93	Cadmium	2·43
Gold	2·93	Mercury	2·39
Copper	2·91	Calcium	2·40
Sodium	2·84	Indium	1·86
Magnesium	2·76	Aluminium	1·25
Lead	2·76		

Indium and Aluminium thus show a tendency to form more complex molecules when dissolved in tin.

Experiments on concentrated solutions.

The importance of experimentally examining Van 't Hoff's theory has directed special attention to dilute solutions, but the effect of increasing concentration on the freezing points of non-electrolytes has been studied by many observers, among others by

[1] *Chem. Soc. Journ.* 1889, 1890.

Beckmann[1], Eykman[2], Raoult[3] and Ponsot[4]. They find that in almost all cases the curves drawn with the concentrations in a given mass of solvent as abscissae and the molecular depressions as ordinates are nearly straight lines, inclined at a small angle with the axis of the abscissae. In some few cases the molecular depression decreases fast as the concentration increases, and, at high concentrations, may even be reduced to half its former value. If we extend our method of calculating molecular weights to such solutions, the result indicates that the molecular weight has doubled at the high concentration, so that polymerisation must have occurred. These cases are few; they include such solutions as those of acetoxim and alcohol in benzene, and must be considered analogous to the polymerisation of gaseous nitrogen peroxide at moderate temperatures.

In general the change of molecular depression is far less than in these solutions, and is probably analogous to the variation from the usual laws shown by gases at high pressures, rather than to a case of gaseous polymerisation. The best value for the molecular weight at infinite dilution would obviously be obtained by producing the curve showing the depression of the freezing point till it cut the axis of no concentration. It is probable that the small deviations of Raoult's numbers for non-electrolytes from the calculated values would become still smaller if this correction for concentration were applied to his observations.

The variation from their ideal laws of gases at high pressures can be approximately expressed by Van der Waals' formula

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

where the pressure p is changed by a term proportional to the molecular attraction (a) and inversely proportional to the

[1] *Zeits. f. physikal. Chemie*, II. p. 715 (1888).
[2] *Zeits. f. physikal. Chemie*, IV. p. 497 (1889).
[3] *Comp. Rend.*, April and November, 1897; *Cryoscopie*, Paris, 1901.
[4] *Ann. de Chem. et Phys.* [7] x. 79 (1897).

square of the volume, and the effective volume v is diminished by a constant b which, according to the theory, is equal to four times the actual volume occupied by the molecules themselves. An equation of the same nature has been developed by Ostwald, Bredig and Noyes, taking account of the molecular volumes of the solvent and of the substance dissolved, and of the interactions between them. In general these latter are very small, and the formula reduces to

$$p(v - d) = K \quad \text{.....(16),}$$

where the constant d expresses a correction for volume, which depends on the nature both of the solvent and of the substance in solution. On the assumption that the depression of the freezing point is proportional to the osmotic pressure, the results deduced from this equation give the linear relation for the freezing point curves found in the experiments described above.

Experiments on the effect of concentration on the freezing points of electrolytes will be considered in a future chapter; but from the most recent results of Ponsot and Raoult on the aqueous solutions of non-electrolytes the following examples may here be quoted.

Cane Sugar. $C_{12}H_{22}O_{11} = 342{\cdot}18$.

(Ponsot. Mean values.)

Gram-equivalents of sugar		Depression of freezing point (δT)	$\delta T/n$	$\delta T/n'$
per thousand grams of water (n)	per thousand grams of solution (n')			
·0287	·0284	·054	1·88	1·89
·0742	·0723	·140	1·89	1·93
·2219	·2063	·419	1·89	2·03
·7358	·5878	1·430	1·94	2·44
1·3823	·9384	2·941	2·13	3·13

(Raoult.)

n	δT	$\delta T/n$
·0284	·0532	1·87
·0652	·1230	1·89
·1250	·2372	1·90
·2499	·4806	1·92
·5054	·9892	1·96
1·0102	2·0897	2·07

Alcohol. $C_2H_6O = 46·05$.

n	δT	$\delta T/n$
·0328	·0600	1·830
·0660	·1207	1·829
·1292	·2367	1·832
·2595	·4760	1·834
·5251	·9645	1·837
1·0890	1·9900	1·828

The behaviour of very strong aqueous solutions has been examined by Pickering[1] who finds the following molecular depressions produced by n molecules dissolved in 100 molecules of solvent.

Substance	$n=1$	5	10	50	100	300	1000	2000
Solvent = Water								
Methyl alcohol	1·05	1·05	1·05	1·03	0·825			
Ethyl „	1·10	1·06	1·15	0·815	0·548			
Acetic acid	1·04	0·944	0·865	0·52				
Solvent = Benzene								
Methyl alcohol	0·6	0·31	0·22	0·077	0·055	0·042	0·040	0·031
Ethyl „	0·6	0·33	0·22	0·10	0·076	0·067	0·044	0·038

[1] *Chem. Soc. Journ. Trans.* LXIII. p. 998 (1893).

The difference between the results obtained by measuring the concentration by the number of gram-molecules of solute per 1000 grams of solution and measuring it by the number of gram-molecules per 1000 grams of solvent, is well shown by the tables and diagrams given by Ponsot, who has determined the freezing points of many concentrated solutions. A higher value for the molecular depression is always obtained by using the former method, and as the concentration increases the difference becomes very great indeed.

CHAPTER VII.

THEORIES OF SOLUTION.

Thermodynamics as a basis for physical science. Application to the case of solution. Theory of direct molecular bombardment. Theory of chemical combination. Conclusion.

THE results obtained in the last two chapters show that the osmotic phenomena can, by the aid of the principles of energetics, be deduced for volatile solutes, and hence extended to other cases. The investigation may start either from the experimental solubility law of gases, or from general molecular theory, which supposes the solute to exist as a number of discrete particles each immersed in and surrounded by the mass of the solvent.

Thermodynamics as a basis for physical science.

By the first of these methods it is possible to develop the theoretical relations of the subject without involving the molecular hypothesis. Such treatment, using as its sole principle of coordination the law of available energy, ultimately rests on the experimental impossibility of perpetual motion.

This way of treating physical science has recently been adopted by a certain number of chemists, as a means of presenting their subject without applying to it the language or conceptions of the atomic theory, in terms of which even its simplest experimental facts have come to be expressed. It may be granted that students have become too apt to ascribe purely hypothetical properties to atoms and molecules,

and that it is often instructive to carry Dalton's atomic theory as far as possible merely as a principle of chemically equivalent weights. But a body of doctrine, based on the statical theory of energy alone, will be limited in its scope, and cases in which it ceases to be sufficient are soon reached. For instance, the phenomena of highly rarefied gases have only been successfully interpreted by the aid of strictly molecular conceptions. While the gases are dense enough to be treated as matter in bulk, their characteristic equations can be constructed from their behaviour with regard to pressure, temperature, etc., and then their other relations can be deduced from the principles of thermodynamics. But this method offers no explanation of the identity of the physical constants for different gases, and also for substances in dilute solution. In such matters we are driven back to molecular theory, which offers an alternative method, equally definite, if in some ways more speculative, of correlating the phenomena.

Application to the case of solution.

In considering the subject of osmotics, the same alternatives appear. The theory can be developed from experimental facts by the principles of energetics alone, or it can be obtained by the application of the fundamental ideas of the molecular theory combined with the laws of energetics. Now, whichever method we adopt, the resulting relations do not depend in any way on the physical mode of action of the osmotic pressure; conversely, therefore, the agreement of the results with observation throws no light on the physical cause of osmotic pressure or the fundamental nature of the state of a dissolved substance. It has often been supposed that the analogy between the laws of the gaseous and osmotic pressures in dilute systems, and still more the identity in the absolute values of those pressures, implies a corresponding identity in their physical nature. But it is now evident that no such conclusion can legitimately be drawn. Whatever the cause of the pressure or the nature of solution may be, they must, by the principles of thermodynamics, have the properties which have been theoretically deduced from known facts and experimentally confirmed. If

we do not accept this result as a sufficient explanation, but wish to analyse the phenomena further, we must regard the exact physical method by which osmotic pressure is produced as still a subject of enquiry.

Two possibilities have been suggested. First, that, like gaseous pressure, osmotic pressure is due to the impacts of the dissolved molecules on the walls of the membrane, which is impervious to them and permeable to the molecules of the solvent; second, that the cause of the pressure is the force of chemical affinity between the solute and the solvent, which tends to make more solvent enter a solution. It may be, however, that these two views will shade into each other in course of development.

Theory of direct molecular bombardment.

On the theory of direct molecular bombardment, the phenomena of the osmotic cell are exactly analogous to those of the diffusion of gases. When a mass of gas is placed in an empty vessel, it finally, if the small effects due to gravity are negligible, distributes itself equally throughout the volume. This result at once follows from the molecular theory, for the particles of which the gas is composed are imagined as always in rapid motion, though with very short free paths. If then we suppose that an imaginary partition is placed anywhere in the gas, the number of molecules crossing it in one second from left to right will be proportional to the number present in unit volume (i.e. the concentration) on the left-hand side, and the number crossing from right to left proportional to the number per unit volume on the right. If the concentration is greater on one side than the other, more molecules will leave that side per second than enter it, and thus the concentration will be reduced till it is equal on both sides. A similar process goes on in the case of a substance dissolved in a liquid: uniformity of distribution is finally reached, though here the difficulties put in the paths of the dissolved molecules by the presence of the denser solvent prevent their travelling fast, and make the process of diffusion very slow.

In the case of mixed gases it is found that the final state

of distribution of one gas is not affected by the presence of another. Thus the amount of aqueous vapour which diffuses from water into a vacuum, is sensibly the same as if the empty space previously contained air, though in this case the process of diffusion is slower. This too is obviously a necessary consequence of the molecular theory, for, provided the molecules are on the whole too far apart to exert mutual influence, the dynamical equilibrium of water and its vapour will not be affected by the presence of molecules of air.

Encounters between the molecules of a gas are continually taking place, and the average energy of translation of each molecule becomes on the whole the same, though sometimes the molecule may be travelling faster and sometimes slower than the average. This can be proved to hold good even if the molecules are of different kinds, as in a mass of mixed gas—the average energy of each is still the same; thus light molecules will travel faster than heavy ones and will therefore diffuse more quickly. This result can be illustrated by the familiar experiment of filling a closed porous pot with air and surrounding it by an atmosphere of hydrogen or coal gas. The molecules of hydrogen enter more rapidly than the heavier ones of air go out, and a pressure gauge will show that the pressure inside the pot becomes greater than outside.

If we could in any way entirely prevent the air from ultimately becoming equalized inside and out, we could get a permanent increase of pressure, for the hydrogen would enter till its concentration was the same within as without. The corresponding phenomenon actually occurs in the case of liquids and is shown by osmotic pressure, which can, as we have described, be demonstrated by the use of membranes which are practically semi-permeable in the manner required.

Let us place a solution of some substance, cane sugar for example, inside a semi-permeable cell, and immerse it in pure water. The molecules of liquid will strike the walls of the membrane on both sides, but since there are both sugar and water molecules inside, fewer water molecules will, in a given time, hit the wall inside than outside. More water molecules pass in therefore than go out, and since none of the sugar can

escape, an internal pressure is produced which can be measured by any convenient gauge. The process will go on until the pressure due to the water is the same on both sides: the excess of pressure may then be regarded as due to the sugar alone. Sugar is here chosen because little or no contraction in volume occurs when it is dissolved, or when the solution is diluted, which makes the theory of the subject much less complicated than in other cases. The simple physical explanation of colliding molecules gives, at any rate, some idea of a possible mode of action of the phenomena.

In most cases, even on this theory, the osmotic pressure, as experimentally measured, must involve other properties which cause a diminution in the available energy of the system on dilution. There may be, for example, a change of volume, or a certain amount of chemical action between the solvent and the dissolved substance, as well as the pressure due to the bombardment of the molecules in solution. When equilibrium is attained, the available energy of the whole system must have reached a minimum value.

For very dilute solutions, however, the cause of osmotic pressure is, on this hypothesis, referred simply to bombardment; and Boltzmann, on special assumptions required for the extension to liquids of the methods of the kinetic theory of gases, has offered a demonstration of the law of osmotic pressure on the basis that the mean energy of translation of a molecule shall be the same in the liquid as in the gaseous state at the same temperature[1]. Such an extension of the bombardment theory to liquids seems however vague and speculative, and, as has been often pointed out by Lord Kelvin and others, the similarity in the mathematical laws of gases and dilute solutions does not necessarily connote identity of physical nature.

Theory of chemical combination.

The alternative theory of the nature of solution already mentioned, refers osmotic pressure to something resembling chemical affinity, which tends to make solvent enter the osmotic cell and combine with the solution. There are two varieties of this theory to be

[1] *Zeit. phys. Chem.* VI. 478 (1890).

considered. There is what is often called the hydrate theory; and there is the view that each particle of solute unites with or influences in some way a large and uncertain number of solvent molecules, thus forming a mobile and somewhat loosely constructed molecular complex, which constantly interchanges its parts with those of other similar complexes.

The hydrate theory imagines that definite hydrates exist in solution, the hydrates being chemical compounds of the solute with water, which, like other chemical compounds, agree with the laws of definite and multiple proportions. As more solvent is added, new compounds containing a larger number of water molecules are formed, and the mixture of these different hydrates allows the continuous variation of composition which is found in solutions.

Theories based on these ideas have been recently framed by H. E. Armstrong[1], S. U. Pickering[2] and others. Pickering supposes that, when solvent is frozen out, some of the existing hydrate is decomposed, and the next lower one formed. From the heats of dilution of solutions of sulphuric acid of different strengths, he calculates the work required to do this, and, adding it to that required to compress the molecules dissolved, deduces the lowering of freezing point[3]. The agreement of his numbers with observation shows that the excess of freezing point depression can be calculated from the heat of dilution, but does not decide whether that heat of dilution is due to the combination with additional molecules of water or (partly at any rate) to the resolution of some sulphuric acid molecules into their ions.

Pickering's main argument for the existence of hydrates in solution is however based on the sudden changes in curvature, first noticed by Mendeléeff, which appear in the lines drawn to represent the variation of some physical property with the concentration. He has made, for instance, a long and careful determination of the densities of sulphuric acid solutions of different strengths, and drawn a curve to show his results.

[1] *Proc. R. S.* No. 243 (1886).

[2] For general account see Watts' *Dict.*, Art. *Solutions*, II.

[3] *B. A. Report*, 1890, p. 320.

Changes of curvature appear at points corresponding to definite molecular proportions (e.g. $H_2SO_4 . H_2O$ and $H_2SO_4 . 4H_2O$). These changes can be more readily seen if a new curve is drawn connecting the concentration with the rate of change of density with concentration (i.e. with the slope at different points of the first curve). By this process of "differentiation" a series of straight lines is obtained with breaks at the positions where, in the first curve, changes of curvature appeared. Similar figures were drawn for electric conductivity, expansion by heat, contraction on formation, heat of dissolution, heat capacity, refractive index, magnetic rotation, and freezing point, and changes of curvature were found at the same points for all. Ostwald however says[1] that the position of the breaks alters with change of temperature. With weak solutions it is impossible to say whether such points correspond to definite molecular proportions, owing to the smallness of the change in percentage composition which would be caused by the addition of another water molecule to H_2SO_4; but the breaks are found of precisely the same character as in the case of stronger solutions, and are, apparently, due to the same cause. The thermal change, resulting from dilution of a strong solution, is usually of the same sign as that obtained by dissolving the solid in the first instance, and this also indicates that, if hydrates are present in concentrated, they are also present in dilute, solutions. If we allow this, it follows that one acid molecule is able to combine with, or at all events to influence in some way, an enormous number of water molecules.

Several hydrates, before unknown, were indicated by the presence of these breaks, and subsequently obtained in the solid form. Thus Pickering isolated $H_2SO_4 . 4H_2O$, $HBr . 3H_2O$, $HBr . 4H_2O$, $HCl . 3H_2O$, $HNO_3 . H_2O$ and $HNO_3 . 3H_2O$. He considers that the crystallization of a definite hydrate is strong evidence that it exists in solution, for bodies suddenly formed at the instant of precipitation come down as amorphous substances—a common observation in the processes of chemical analysis. Dilute sulphuric acid, dissolved in acetic acid, produces a smaller depression of the freezing point than the sum

[1] Watts' *Dict.*, Art. *Solutions*, I.

of those due to the acid and water separately, hence Pickering argues that no dissociation, but rather chemical union, resulting in a reduction in the number of molecules, has occurred.

The combination of large numbers of solvent molecules with one molecule of a body in solution may produce forces equal in all directions and thus secure the mobility of the dissolved molecules. Certain definite numbers of solvent molecules will be capable of more symmetrical arrangement than others, and will form hydrates, but their parts are freely interchangeable with each other. A dissolved molecule will be able to pass through a crevasse only when the number of solvent molecules requisite to keep it in solution can pass simultaneously, and this may explain the action of semi-permeable membranes. Pickering, as described on p. 97, found that, when a mixture of propyl alcohol and water was placed in a porous pot, and the whole immersed either in pure water or pure alcohol, the volume of liquid inside the porous pot increased, showing that the phenomenon is due, not to the impermeability of the pot to either constituent alone, but to its impermeability to the solution as a whole.

On the other hand, it may be argued that the evidence in favour of the existence of definite hydrates in the liquid phase is inconclusive, for the study of saturated solutions as special cases of systems in equilibrium, which has been made in the early chapters of this book, shows that it does not follow because a definite solid crystallizes from a solution, that it must necessarily exist in the same state of molecular aggregation in the liquid phase.

The general analogy between the process of solution and cases of definite chemical action is, nevertheless, very close; and it was accepted as a real identity[1] till the development of osmotic theory by Van 't Hoff showed the similarity between solutions and gases, and thus caused more stress to be laid on that aspect of the subject. There is evidence to show that chemical action does not always result in the formation of compounds in which the usual valencies of the elements present are exactly satisfied. The fact that salts often combine

[1] Tilden, *B. A. Report*, 1886, p. 444.

with one or more molecules of water to form definite crystalline hydrates is an instance of this property, and the phenomena have been extensively studied by chemists, sometimes under the name of residual affinity, the resultant substances being usually known as molecular compounds. From such bodies as these to the mobile aggregations required by the molecular complex view of solution is no impossible step. It is easy to imagine a loose kind of chemical union in which the continuously variable compositions and the general mobility characteristic of solutions might be realized, but the chief difficulty in the way of such a chemical theory has been its inability to suggest a probable mechanism by which the equality in absolute values of the osmotic and gaseous pressures would necessarily follow.

The same difficulty has confronted the theory of definite chemical compounds, but in the year 1896 Poynting showed that, if certain assumptions were made, the observed result would follow[1]. Let us consider the effect of combination on the vapour pressure. "If the molecules of salt were simply mixed with those of the solvent, or if they combined to form stable non-evaporating compounds with the solvent, which compounds were simply mixed, then the mixture should have the same vapour pressure as the pure solvent. For we might regard the salt or compound molecules at the surface as equally reducing the effective evaporating and the effective condensing area, somewhat as a perforated plate or gauze laid on the surface would do. But the salt probably combines with the solvent to form unstable molecules which continually interchange constituents, so that when near the surface they may serve equally with those of the pure solvent to entangle the molecules of vapour coming downwards, these descending vapour molecules taking the place of molecules attached to the salt. Probably, however, they are less energetic than the pure solvent molecules and do not contribute so much to evaporation. We shall make the supposition that they do not contribute at all." It may be observed that the same result will be reached if each salt molecule diminishes the facility for evaporation of x solvent molecules by the $1/x$th part.

[1] *Phil. Mag.* XLII. 298 (1896).

If N is the number of gram molecules of solvent per litre and n the number of gram-molecules of solute, the number of solvent molecules left unaffected is $N-n$. There are then N molecules active for condensation, and only $N-n$ active for evaporation. Hence the vapour pressure is reduced in the ratio $(N-n)/N$. Thus

$$\frac{p'}{p} = \frac{N-n}{N}$$

and

$$\frac{p-p'}{p} = \frac{n}{N},$$

which is the relation already deduced on p. 130, from the known value of the osmotic pressure. Conversely, this last result yields the true osmotic law by an inversion of the process there used.

Reasons have already been stated for believing that the osmotic pressure is proportional to the number of spheres of influence of solute particles immersed in the solvent, and therefore that, in solutions of electrolytes, which have abnormally great osmotic pressures, partial dissociation must occur, resulting in an increase in the number of such effective particles. Later, we shall find that a similar dissociation is indicated by the facts of electrolysis, which lead to the conclusion that some of the molecules of salts, etc. are resolved into two or more parts by the act of solution, and that these parts, or ions as they are called, travel through the liquid in opposite directions under the action of an electromotive force and are therefore charged electrically. The two independent lines of enquiry thus lead to the same hypothesis of electrolytic dissociation, and the evidence for and against this theory will have to be fully considered in future chapters.

On Poynting's view of osmotic pressure then, as the writer has previously indicated[1], the supposition of combination between the solute and the solvent has to be extended to include the case where the solute is resolved into its ions. We must imagine that each ion itself destroys the facility for evaporation of one solvent molecule, or diminishes that facility in like proportion in a group of solvent molecules, just as each molecule

[1] *Nature*, LIV. 571; LV. 33 (1896).

of a non-electrolytic solute does[1]. With this extension, the theory of chemical combination seems to agree with the facts.

Conclusion.

There are thus different views as to the nature of solution, each offering a reasonable explanation of the phenomena. At first sight, the idea of molecular bombardment on the walls of the membrane by solute particles which are dynamically independent of the solvent molecules seems diametrically opposed to the hypothesis of chemical combination between them; but we know too little about the nature of chemical affinity to be quite sure that it is not due to some relation in the dynamical properties of the reagents, and the two views of solution may after all be different statements of the same truth.

However this may be, the two theories at present stand opposed, and each seems capable of explaining the ordinary facts of osmotic pressure. These phenomena, therefore, are unable to provide a crucial experiment to decide between the hypotheses. It will, however, be noticed that Pickering's experiment, in which either propyl alcohol or water enters as solvent an osmotic cell containing a mixture of these two liquids, seems to show that it is to a combination that the membrane is impervious, and is thus in favour of the view that solution is due to something analogous to chemical action.

It must be clearly understood that an enquiry about the nature of solution and the physical mode of action of osmotic pressure is a problem entirely distinct from that of the essential difference between an electrolyte and a non-electrolyte. The hypothesis of ionic dissociation is quite independent of the direct bombardment theory of osmotic pressure, with which it has often been confused, and is perfectly consistent with the view that solution is a process of the same ultimate nature as ordinary chemical action. Stress is laid on this point, because criticisms of the direct bombardment theory of osmotic pressure have sometimes been adduced as reasons for refusing to accept the idea of the ionic dissociation of electrolytes[1].

[1] For a controversial discussion of these questions see *Nature*, LIV., LV., indexed under "Osmotic Pressure," "Ions, theory of," etc.

CHAPTER VIII.

ELECTROLYSIS.

Introduction. Volta's pile. Early experiments. Faraday's work. Polarization. Faraday's laws. Electrochemical equivalents. The electrolysis of gases. Nature of the ions.

Introduction.

THE origin of the study of electrolysis is to be found in the work of Galvani at Bologna. About the year 1786 he noticed that the leg of a frog contracted under the influence of a discharge from an electric machine. Following up this discovery, he observed the same contraction when a nerve and a muscle were connected with two dissimilar metals, placed in contact with each other. Galvani attributed these effects to a so-called animal electricity, and it was left for another Italian, Volta of Pavia, to show that the essential phenomena did not depend on the presence of an animal substance. In 1800 Volta invented the pile still known by his name, which, by reason of the greater intensity of its action, provided a means of investigation that was at once put into use by himself and his contemporary workers in other countries.

Volta's pile.

Volta's pile consisted of a series of little discs of zinc, copper and blotting-paper moistened with water or brine, placed one on top of the other in the order zinc, copper, paper, zinc, etc., finishing with copper[1].

[1] Volta thought that the origin of the effects was at the junction of the two metals, hence the order of discs in the pile, and the terminal metal plates in air in the crown of cups. These plates are now known to be useless.

Such an arrangement is really a primitive primary battery, each little pair of discs separated by moistened paper acting as a cell, and giving a certain difference of electric potential, the differences due to each little cell being added together and producing a considerable difference of potential or electromotive force between the zinc and copper terminals of the pile. Another arrangement was the crown of cups, consisting of a series of vessels filled with brine or dilute acid, each of which contained a plate of zinc and a plate of copper. The zinc of one cell was fastened to the copper of the next and so on, the isolated copper and zinc plates[1] in the first and last cups forming the terminals of the battery.

Volta arranged the metals in an electromotive series so that, when placed in a solution, a metal is always positive to any of those below it in the series and negative to those above it. J. W. Ritter pointed out that the order of this list is also the order in which the metals precipitate each other from solution, an important connexion between electrical and chemical phenomena only appreciated long afterwards.

Volta also discovered that the same difference of potential is given by two metals, whether they are directly connected, or joined by means of a third metal. Thus, in any complete circuit made up of a number of different metals, the total electromotive force must vanish.

Early Experiments.

Using a copy of Volta's original pile, Nicholson and Carlisle[2] found that when two brass wires leading from its terminals were immersed near each other in water, there was an evolution of hydrogen gas from one, while the other became oxidised. If platinum or gold wires were used, no oxidation occurred, but oxygen was evolved as gas. They noticed that the volume of hydrogen was about double that of oxygen, and, since this is the proportion in which these elements are contained in water, they explained the phenomenon as a decomposition of water. They also noticed

[1] See note, p. 176.

[2] *Nicholson's Journal*, IV. p. 179 (1800).

that a similar kind of chemical action went on in the pile itself, or in the cups when that arrangement was used. Cruickshank[1] soon afterwards decomposed the chlorides of magnesia, soda and ammonia, and precipitated silver and copper from their solutions—an observation which afterwards led to the process of electroplating. He also found that the liquid round the pole connected with the positive terminal of the pile became alkaline and the liquid round the other pole acid. In 1806 Sir Humphry Davy[2] proved that the formation of the acid and alkali was due to impurities in the water. He had previously shown that decomposition of water could be effected although the two poles were placed in separate vessels connected together by vegetable or animal substances, and established an intimate connexion between the galvanic effects and the chemical changes going on in the pile. The identity of "galvanism" and electricity, which had been maintained by Volta, and had formed the subject of many investigations, was finally established in 1801 by Wollaston, who showed that the same effects were produced by both, while in 1802 Erman measured with an electroscope the potential differences furnished by a voltaic pile.

In 1804 Hisinger and Berzelius[3] stated that neutral salt solutions could be decomposed by electricity, the acid appearing at one pole and the metal at the other, and drew the conclusion that nascent hydrogen was not, as had been supposed, the cause of the separation of metals from their solutions. Many of the metals then known were thus prepared, and in 1807 Davy decomposed potash and soda, which had previously been considered to be elements, by passing the current from a powerful battery through them when in a moistened condition, and so isolated the metals potassium and sodium.

The remarkable fact that the products of decomposition appear only at the poles was perceived by the early experimenters on the subject, who suggested various explanations.

[1] *Nicholson's Journal*, IV. p. 187.

[2] Bakerian Lecture for 1806, *Phil. Trans.*

[3] *Ann. de Chimie*, LI. p. 167 (1804).

Grotthus[1] in 1806 supposed that it was due to successive decompositions and recombinations in the substance of the liquid. Thus if we have a compound AB in solution, the molecule next the positive pole is decomposed, the B atom being set free. The A atom attacks the next molecule, seizing

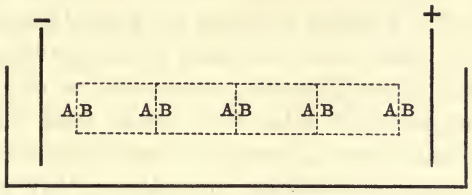


Fig. 46.

the B atom and separating it from its partner which attacks the next molecule and so on. The last molecule in the chain gives up its B atom to the A atom separated from the last molecule but one, and liberates its A atom at the negative pole.

Faraday's work.

Grotthus, and other pioneers in the subject, thought that the decomposition was due to a direct attraction exerted by the poles on the opposite constituents of the decomposing compound, which varied as the square or some other power of the distance. This explanation of electrolytic action, as framed by the early experimenters, was finally disproved by Faraday[2], who placed two platinum strips, kept at a constant difference apart and connected through a galvanometer, at different positions in a trough of dilute acid through which a current was flowing. The deflection of the galvanometer was the same for all positions of the strips, thus showing that the electric forces were the same everywhere between the poles. He also showed that chemical decomposition could be produced without the presence of any metallic pole. An electric discharge from a sharp point connected with a frictional machine, was directed on to a strip of turmeric

[1] *Ann. de Chimie*, LVIII, p. 54 (1806).
[2] *Experimental Researches*, 1833.

paper moistened with sulphate of soda solution, the other end of the paper being joined to the other terminal of the machine. Alkali appeared on the paper opposite to the discharging point. Another experiment showed that insoluble hydrate of magnesia was produced at the junction between a strong solution of sulphate of magnesia and pure water when a current was passed across it. Faraday accepted the idea of Grotthus' chain, but held that there were chemical forces between atoms of opposite kinds in neighbouring molecules as well as in the same molecule, and that when the electric force was added to these they became strong enough to overcome the attractions between the atoms in the same molecule, so that a transfer of partners occurred. We shall see later that transfers of partners are probably always going on in solutions, whether a current is passing or not, and that the function of the electric forces is merely directive, but Faraday's account of the consequences of this interchange still holds good. He pointed out how it explained all the facts, including the passage of acids through alkalies under the influence of the current, a phenomenon which had created great surprise when discovered by Davy. Faraday remarked that the presence of the alkali not only facilitated the passage of the acid, but was even necessary, for, without something with which to combine on its way, the acid would be unable to travel. Thus Faraday's view amounts to supposing a constant stream of acid in one direction and of alkali in the other.

Faraday introduced a new terminology which is still used. Instead of the word *pole* which implied the old idea of attraction and repulsion, he used the word *electrode*, and called the plate of higher electric potential, by which the current is usually said to enter the liquid, the *anode*, and that by which it leaves the liquid, the *cathode*. The parts of the compound which travel in opposite directions through the solution he called *ions*—*cations* if they went towards the cathode and *anions* if they went towards the anode. He also introduced the words electrolyte, electrolyse, etc., which we have already used.

Faraday pointed out that the difference between the effects

of a frictional electric machine and of a voltaic battery lay in the fact that the machine produced a very great difference of potential, but could only supply a small quantity of electricity, while the battery gave a constant supply, much larger in quantity, but only produced a very small difference of potential.

Polarization.

The diminution with time of the intensity of the voltaic pile or cell was noticed by the early observers, and was investigated by Davy and Faraday. The researches of the latter physicist brought out its connexion with the accumulation at the electrodes of the products of the decomposition of an electrolyte through which a current is passed. Faraday showed that a definite minimum "intensity," depending on the nature of the electrolyte, was necessary for the ions or their products to be liberated at the electrodes. He arranged certain substances in the order of what we should now term their decomposition voltages, and pointed out the relation between this order and that in which the same bodies could be placed with reference to the intensity of secondary current they would furnish when disconnected from the primary battery and then joined with a galvanometer. This phenomenon, originally observed by Ritter, lies at the base of the action of the accumulator.

When the intensity of the primary current is not enough to visibly decompose an electrolyte, Faraday showed that a small current still passed. Whether this leakage current really flows without chemical separation at the electrodes, or is kept up by the removal of the products of the action as fast as they are formed, is a question to be considered later.

When the nature of the electromotive force of a battery was more generally understood, it was evident that Faraday's work showed that the reverse electromotive force of "polarization," as the phenomenon under consideration was named, must be subtracted from the primary electromotive force of the battery, before the effective electromotive force of the system could be calculated.

The injurious effects of polarization in primary batteries led to many attempts to overcome it. The methods in use in the common form of cell are well known. They can be classed in three groups, according as their action is:

(1) mechanical, as in Smee's cell, where the silver plate is covered with crystals of platinum, the sharp edges of which aid the escape of the hydrogen evolved;

(2) chemical, as in the bichromate cell, where the hydrogen is converted into water by an oxidising agent; or

(3) electrochemical, as in Daniell's cell, where the hydrogen ions enter a solution of copper sulphate, and are therefore replaced on the electrode by copper, which has a lower decomposition voltage.

Faraday's Laws.

Davy had previously shown that there was no accumulation of electricity in any part of a voltaic circuit, and that a uniform flow or current existed throughout. Faraday set himself to examine the relation between the strength of this current and the amount of chemical decomposition. He first proved by observations on the decomposition of acidulated water, that the amount of chemical action in each of several cells was the same when the cells were joined together and a current passed through them all in series, even if the sizes of the platinum plates were different in each. The volume of hydrogen was unchanged even if electrodes of different materials—such as zinc or copper—were used. He then divided the current after it had passed through one cell into two parts, each of which passed through another cell before being reunited. The sum of the volumes of the gases evolved in these two cells was equal to the volume evolved in the first cell. The strength of the acid solution was then varied, so that it was different in the different cells in one series, but the chemical action still remained the same in all. Thus the induction known as Faraday's first law was made:—

The amount of decomposition is proportional to the quantity of electricity which passes.

An apparatus for the decomposition of water can therefore be used to measure the total quantity of electricity which has passed round a circuit. Such instruments are termed voltameters.

The same law was then shown to be true for solutions of various metallic salts, and also for salts in a state of fusion—the weight of metal deposited being always the same for the same quantity of electricity. A second law also was formulated:—

The mass of an ion liberated by a definite quantity of electricity is proportional to its chemical equivalent weight.

In the case of elementary ions this equivalent weight is the atomic weight divided by the valency, and in the case of compound ions it is the molecular weight divided by the valency.

It was then proved that the amount of zinc consumed in each cell of the battery was identical with that deposited by the same current in an electrolytic cell placed in the external circuit.

Faraday's work laid the foundations of the modern quantitative science of electrolysis. His results can be gathered into one statement, as follows:—

The quantity of a substance which separates at an electrode is proportional to the whole amount of electricity which passes and to the chemical equivalent weight of the substance.

This statement implies that no current flows without a corresponding amount of chemical separation at the electrodes. Faraday himself thought that, in certain cases, a small current could leak through electrolytes without causing separation, a point which cannot yet be regarded as settled. In the case of the electrolysis of solutions in water of metallic salts, such as those of silver, copper, etc., experiments seem to show that there is no leakage current, and that the deposition of metal or the evolution of gas is strictly proportional to the electric transfer as long as the electromotive force is high enough to overcome the reverse force of polarization, which is generally present in cases of electrolysis. When a smaller electromotive

force than this is applied, the current flows at first, but its strength gradually diminishes, until finally it almost vanishes. The cause of the slight leakage current that then remains will be considered later.

In connexion with this, it is interesting to note that Nernst has recently investigated mixtures of the oxides of certain metals, such as magnesium, zirconium, etc., which conduct well when hot, and give very little chemical decomposition. These substances however show signs of polarization, and are also transparent to light, a property considered incompatible with true metallic conductivity[1]. Again, metallic sodium dissolves in liquid ammonia, giving a conducting solution which shows no polarization and seems to undergo no chemical changes[2]. It is as yet uncertain whether metallic and electrolytic conductivity are ever associated in the same substance, and further experiments are necessary to decide the point.

Electrochemical equivalents.

The confirmation of Faraday's law for solutions of silver salts has been incidentally effected in the course of many experimental determinations of the electrochemical equivalent of silver. If the value obtained for the silver deposited by unit quantity of electricity is the same when the strength of current and the other conditions of the experiment are varied, the quantity of electricity and the mass of silver deposited must be proportional to each other. An exact knowledge of the electrochemical equivalent of silver is of great importance, since, given this constant, a silver voltameter can be used as a means of measuring accurately the total quantity of electricity, or the average current, which has passed through a circuit. This method has been adopted in the determination of the electromotive force of the standard Clark cell, and in several measurements that have been made by electrical means of the thermal equivalent of the unit of mechanical energy.

In order to determine the electrochemical equivalent, a

[1] *Zeits. Elektrochem.* VI. 41 (1899).

[2] Cady, *Jour. Phys. Chem.* I. 710 (1897).

constant current of known strength is passed for a measured time through a solution of some silver salt. The most constant results are obtained when a neutral solution of the nitrate is used containing about fifteen parts of salt to one hundred of water, and the current has an intensity of about one hundredth of an ampère to the square centimetre. The silver may be deposited on a platinum bowl used as cathode, the anode being a silver plate wrapped in filter paper to catch any particles disintegrated. The electrochemical equivalent is expressed as the number of grams of silver deposited by a current of one ampère in one second. The following are perhaps the best determinations of this constant:

Lord Rayleigh and Mrs Sidgwick[1] ...	0·00111795.
F. and W. Kohlrausch[2]	0·0011183.
Pellat and Potier[3]	0·0011192.
Patterson and Guthe[4]	0·0011192.
Richards, Collins and Heimrod[5]	0·0011172.

Thus the mean result is about 0·001118 or 0·001119 grams per ampère-second. The electrical measurements of the thermal equivalent agree better with the mechanical ones if the higher value is taken, and we shall therefore consider that the most probable value in the present state of our knowledge is 0·001119 grams of silver per ampère-second. The corresponding constant for other elements or compounds can be calculated from this number by dividing it by the chemical equivalent of silver, viz. 107·9, and multiplying by the chemical equivalent of the substance required. The value for hydrogen thus comes out $1{\cdot}045 \times 10^{-5}$, its atomic weight being taken as 1·008, when oxygen is 16.

It will be noticed that the chemical constant involved is the equivalent, and not the atomic weight. Therefore, in the

[1] *Phil. Trans.* CLXXV. 411 (1884).
[2] *Wied. Ann.* XXVII. 1 (1886).
[3] *Journal de Physique* [2] IX. 381 (1890).
[4] *Phys. Rev.* VII. 257 (1898).
[5] *Zeit. Phys. Chem.* XXXII. 301 (1900).

case of substances like iron, which form two series of salts, the amounts deposited will be different when solutions of the different salts are used. The two amounts will be in the proportion of the two chemical equivalents; if a current is sent through solutions of a ferric and a ferrous salt in series, the resultant weights will be as 56/3 : 56/2.

With no substance other than silver have such accurate experimental results been obtained, though many observations have been made on copper and other metals in aqueous solutions of their salts. In all cases, Faraday's law has been found to be true within the limits of experimental error, the apparent variations which sometimes appear, especially with copper, having been traced to known causes[1], such as the solubility of the metal in the solution.

The experimental errors are much greater when gases are evolved, as in the electrolysis of acidulated water. The gases are to some extent soluble in the liquid, and may be absorbed in the substance of the electrodes; oxygen is often liberated partly in the condition of ozone, while gases like chlorine attack the liquid or the electrodes, forming chemical compounds with them. Although several direct measurements of the electrochemical equivalent of water have been made, on account of these sources of uncertainty, none of them can be considered as very accurate. Since the general evidence for Faraday's law is very strong, it is better to calculate electrochemical equivalents from the measured value for silver and the known chemical equivalents of the different ions. Kohlrausch and Holborn[2] give a list of equivalent and electrochemical equivalent weights, the experimental value for silver being taken as 1·118 mg./amp.-sec. It is now probable that this number should be raised by one part in a thousand, and the electrochemical equivalents in the following table have all been increased in the same proportion.

[1] W. N. Shaw, *B. A. Report*, 1886, p. 411.

[2] *Leitvermogen der Elektrolyte*, Leipzig, 1898.

Equivalent weights A ($\frac{1}{2}O = 8{\cdot}00$), *and electrochemical equivalents E in mg./(amp.-sec.) of mono- and di-valent ions.*

Cations			Anions		
	A	*E*		*A*	*E*
—	1	0·01037	Cl	35·45	0·3677
H	1·008	0·01045	Br	79·96	0·8291
K	39·14	0·4059	I	126·86	1·3152
Na	23·05	0·2390	Fl	19·05	0·1975
Li	7·03	0·0729	OH	17·01	0·1764
Ag	107·92	1·119	CN	26·04	0·2701
NH_4	18·07	0·1874	NO_3	62·04	0·6433
$\frac{1}{2}Ba$	68·70	0·7124	ClO_3	83·45	0·8653
$\frac{1}{2}Sr$	43·81	0·4544	BrO_3	127·96	1·3269
$\frac{1}{2}Ca$	20·02	0·2076	IO_3	174·86	1·8132
$\frac{1}{2}Mg$	12·17	0·1262	CHO_2	45·01	0·4668
$\frac{1}{2}Zn$	32·7	0·3391	$C_2H_3O_2$	59·02	0·6120
$\frac{1}{2}Cd$	56·05	0·5812	$\frac{1}{2}O$	8·00	0·08296
$\frac{1}{2}Cu$	31·8	0·3297	$\frac{1}{2}S$	16·03	0·1663
$\frac{1}{2}Fe$	28·01	0·2905	$\frac{1}{2}SO_4$	48·03	0·4981
$\frac{1}{2}Mn$	27·5	0·2852	$\frac{1}{2}CrO_4$	58·07	0·6022
$\frac{1}{2}Ni$	29·35	0·3044	$\frac{1}{2}CO_3$	30·00	0·3111
$\frac{1}{2}Pb$	103·46	1·0728	$\frac{1}{2}C_2O_4$	44·00	0·4563
$\frac{1}{2}Cr$	26·07	0·2704	$\frac{1}{2}SiO_3$	38·20	0·3961

Solvents other than water, for example acetone and pyridine, have often been used. Faraday's laws also hold good in such cases, and the electrochemical equivalents seem to be identical with those obtained when the solvent is water[1].

Faraday's laws have also been demonstrated for fused salts, many of which are good electrolytes, with conductivities of the same order as those of aqueous solutions[2].

Again, in recent years it has been shown that the discharge of electricity through gases is an electrolytic process accompanied by chemical decomposition. Here also the same laws describe the phenomena, the electric charge associated with a gaseous ion being the same in amount as the charge on an ion in solution. J. J. Thomson[3] has found that the sign of the

[1] Kahlenberg, *Journ. Phys. Chem.* IV. 349 (1900); and Skinner, *B. A. Report*, 1901.

[2] Faraday, *Experimental Researches*, and Helfenstein, *Zeits. Anorg. Chem.* XXIII. 255 (1900).

[3] *Proc. R. S.* LIII. 90 (1893); LVIII. 244 (1895).

charge depends on the nature of any other ion present. Moreover, it may even be changed by varying the conditions of the experiment: the electrodes at which hydrogen and oxygen are liberated in the electrolysis of steam are reversed when an arc instead of a spark discharge is used.

In every case of electrolysis Faraday's laws seem to apply, and the amount of a given substance liberated by a given transfer of electricity appears to be the same under all conditions. This result leads to an exact view as to the nature of the process. Since the amount of substance deposited is proportional to the quantity of electricity which passes, it follows that a definite charge of electricity is associated with a definite mass of the substance. We are thus led to look on electrolysis as a kind of convection, each ion carrying with it a fixed charge of electricity, positive or negative, which is given up to the electrode under the influence of an electromotive force above a certain limit. It is clear that, on this convective view of electrolysis, the conductivity of a solution must be proportional to the charge on each ion, to the number of ions, and to the velocity with which they move through the solution.

Whenever one gram-atom or gram-molecule of any monovalent ion is separated at an electrode, the same quantity of electricity passes round the circuit; if the ion is divalent, the quantity is twice as great, and so on. All monovalent ions must therefore be associated with the same charge, all divalent ions with twice that charge, etc.

The quantity of electricity involved is easily calculated by considering an example. If a current of one ampère flows for one second, experiment shows that 0·001119 grams of silver are liberated from the solution of one of its salts. Thus, when the equivalent weight in grams is deposited, the quantity of electricity passing is 107·92/0·001119 or 96440 ampère-seconds or coulombs. The same result is of course true for the gram-equivalent of any other substance, the gram-equivalent being the gram-molecule or gram-atom divided by the valency. Whenever a gram-equivalent of a substance is decomposed, therefore, 96440 coulombs of electricity pass round the circuit,

and, as we shall prove later, this is the amount of charge actually transported through the electrolyte by one gram-equivalent of any ion.

It is possible to calculate approximately the absolute electric charge carried by a single monovalent ion, since the number of molecules in a given volume of gas can be estimated by the kinetic theory from the viscosity and diffusion constant. At 0° C. and normal atmospheric pressure, there exist about $2{\cdot}5 \times 10^{19}$ molecules in one cubic centimetre of any gas.

As we have seen, one electromagnetic unit of electricity evolves $1{\cdot}045 \times 10^{-4}$ gram of hydrogen, which at normal temperature and pressure fills a volume of 1·16 c.c., and therefore contains about 3×10^{19} molecules or 6×10^{19} atoms, and yields the latter number of ions when dissolved as a hydrogen salt. Each ion is then associated with $1{\cdot}7 \times 10^{-20}$ electromagnetic units. The ratio between the units of electric quantity being 3×10^{10}, the ionic charge is about 5×10^{-10} electrostatic units.

Another value for the number of molecules of gas can be deduced from the measured variations of the gases from Boyle's law. The kinetic theory here leads to the result $1{\cdot}2 \times 10^{19}$, and the corresponding ionic charge is about 10^{-9} electrostatic units.

The electrolysis of gases.

The charge on the ions produced by the passage of Röntgen rays through gases has been investigated by J. J. Thomson[1]. If N is the number of ions in unit volume of the gas, e the charge on each of them, and v the mean velocity of the positive and negative ions under a given electromotive force, the product Nev can be determined by exposing a gas to the action of Röntgen rays and measuring the current produced through it by a known electromotive force. Rutherford[2] has determined v for a considerable number of gases, and the number N can be estimated by a method due to C. T. R. Wilson, who, as described on p. 43, has shown that gaseous ions act as condensation nuclei in air saturated with aqueous vapour. From the velocity of fall of the cloud so formed, it is possible to calculate the approximate size of the

[1] *Phil. Mag.* XLVI. 528 (1898).
[2] *Phil. Mag.* XLIV. 422 (1897).

resulting drops of water, and from the weight of the drops precipitated their number is known. Assuming that each ion acts as a centre of condensation, this result gives the number of ions present. The measure of the current through the ionized gas then furnishes a value for e the ionic charge equal to about $6{\cdot}5 \times 10^{-10}$ electrostatic units. This result, it will be seen, lies between those reached by the aid of the kinetic theory of gases, and indicates that the ionic charge is the same in this case as it is in liquid electrolytes.

This identity was established in another way by J. S. Townsend[1]. At 15° and normal pressure one electromagnetic unit evolves 1·23 c.c. of hydrogen: if the number of molecules in one cubic centimetre is N, the number of atoms or ions associated with the unit of electricity is $2{\cdot}46N$, so that, if E is the charge on an ion in the liquid electrolyte,

$$2{\cdot}46\ NE = 1 \text{ electromagnetic unit}$$
$$= 3 \times 10^{10} \text{ electrostatic units.}$$

Hence

$$NE = 1{\cdot}22 \times 10^{10} \text{ electrostatic units.}$$

Now, by investigating the rates of diffusion of the gaseous ions produced by the action of Röntgen rays, and using Rutherford's values for the corresponding ionic velocities, Townsend deduced the following results for the product NE in gases:

Air	$1{\cdot}35 \times 10^{10}$,
Oxygen	$1{\cdot}25 \times 10^{10}$,
Carbonic acid	$1{\cdot}30 \times 10^{10}$,
Hydrogen	$1{\cdot}00 \times 10^{10}$,

numbers agreeing with that calculated for liquid electrolytes. Since N is a constant for all gases, it follows that the charges on the ions in these gases are all the same, and equal to the charge on a monovalent ion in a liquid electrolyte.

In all cases in which gaseous ions are produced by the action of Röntgen rays and similar agencies, their charges seem to consist of the same quantity of electricity as that associated with a monovalent ion in a liquid electrolyte. When steam is

[1] *Phil. Trans.* CXCIII. A, 129 (1899).

electrolyzed by an electric spark, the ions of divalent substances like oxygen possess a double charge as they do in liquids, but these larger charges are always simple multiples of the monovalent charge. The quantity of electricity on a monovalent ion seems to be a natural unit, and the results summarized above lead to an atomic theory of electricity. This natural unit of electricity is called an electron. The effect of magnetic and electrostatic forces on their paths gives evidence to show that the negative ions produced by Röntgen rays, etc., are of much smaller mass than hydrogen atoms, while the positive ions are comparable in mass to ordinary molecules. Thomson[1] holds that these negative ions or corpuscles constitute the fundamental basis of all chemical atoms, and are likewise identical with electrons or free charges of negative electricity, a positive ion being produced when one of these corpuscles is removed from any neutral atom or molecule. According to this view, the ions in liquid electrolytes, or in gases through which an electric spark or discharge passes, consist of separated parts of molecules possessing an excess or defect of one electron, and in this way being negatively or positively charged. On the other hand, the ionizing action of Röntgen rays, etc., causes one particle to be detached from the undissociated molecule of the gas, leaving that molecule positively electrified and furnishing a free corpuscle, which constitutes an isolated negative charge or electron.

The nature of the ions.

Speculation as to the nature of the ions began at an early period in the history of electrolysis. In the early years of the nineteenth century, Berzelius, from a prolonged study of the electrolytic decomposition of neutral salts, enunciated a theory that all chemical action was the result of electric forces between oppositely charged atoms. When two atoms united, he supposed that the charges were not exactly neutralised, and the group of atoms was left with a balance of positive or negative electricity, and so could still combine with other atoms or groups of atoms. He regarded

[1] *Phil. Mag.* XLIV. 293 (1897); XLVIII. 547 (1899).

each chemical compound as formed by the union of an electro-positive group with an electro-negative group, and held that the action of the electric current in producing acid round the anode, and alkali round the cathode, of a neutral salt solution, was to be explained simply as a direct separation of the salt into acid and base. When the attention of experimenters was directed to organic chemistry, the dualistic conception of Berzelius was perforce abandoned, and even from the physical side his theories were soon found to need alteration. Thus Daniell showed that in the electrolysis of a solution of sodium sulphate an equivalent of hydrogen was produced as well as an equivalent of acid and base. This is at once reconciled with Faraday's law if we suppose that the parts of the salt, from an electrolytic point of view, are Na and SO_4, and that the hydrogen results from a secondary action of the sodium on the water of the solution.

With simple salts, acids and alkalies, there is seldom any doubt about the character of the ions; the cation is the metal or hydrogen, the anion is the halogen (chlorine, bromine or iodine), a compound acid group (such as SO_4), or hydroxyl HO when the electrolyte is an alkali.

A study of the products of decomposition does not necessarily lead directly to a knowledge of the ions actually involved in the passage of the current through the electrolyte. Since the electric force is active throughout the whole solution, all the ions must come under its influence and therefore move, but their separation from the electrodes is determined by the electromotive force needed to liberate them. Therefore as long as every ion of the solution is present in the layer of liquid next the electrode, the one which responds to the least electromotive force will alone be set free until the amount of this ion becomes too small to carry all the current across the junction layer, when the other ions begin to appear. In aqueous solutions, a few hydrogen and hydroxyl ions derived from the water are always present, as we shall see later, and will be liberated if the other ions require a higher electromotive force and the current be kept small.

The issue is also obscured in another way. When the ions

are set free at the electrodes, they may unite with the substance of the electrode or some constituent of the solution and form secondary products. The hydroxyl mentioned above decomposes into water and oxygen, and the chlorine produced by the electrolysis of a chloride may attack the metal of the anode.

This leads us to examine more closely the part played by water in electrolysis. It was at first thought to be the only active body, and to be necessary in every case of electrolytic decomposition. The dilute acid or alkali which was always added when water was to be decomposed, was supposed merely to allow the passage of the current by reason of its conductivity, and it was imagined that the current then directly decomposed the water. Now pure water is known to be a very bad conductor, though when great care is taken to remove all dissolved bodies, there is evidence to show that some part of the small trace of conductivity remaining is really due to the water itself. Thus F. Kohlrausch[1] has prepared water the conductivity of which as compared with that of mercury was $1{\cdot}8 \times 10^{-11}$ at 18° C. Even here some little impurity was present, and Kohlrausch estimates that the conductivity of chemically pure water would be $0{\cdot}36 \times 10^{-11}$ at 18° C. As we shall see later, the conductivity of very dilute salt solutions is proportional to the concentration, so that it is probable that in most cases practically all the current is carried by the salt. At the electrodes, however, the small quantity of hydrogen and hydroxyl ions from the water are first liberated in cases where the ions of the salt have a higher deposition voltage. The water being present in excess, the hydrogen and hydroxyl are at once re-formed, and therefore constantly liberated. If the current is so strong that new hydrogen and hydroxyl ions cannot be formed in time, other substances are liberated; in a solution of sulphuric acid, a strong current will evolve sulphur dioxide, the more readily as the concentration of the solution is increased. Similar phenomena are seen in the case of a solution of hydrochloric acid in water. When the solution is weak, hydrogen and oxygen are evolved; but, as the concentration is

[1] *Wied. Ann.* LIII. 209 (1894).

increased, and the current raised, more and more chlorine is liberated. We shall return to this point in a later chapter in connexion with the study of decomposition voltages.

An interesting example of secondary action is furnished by the common technical process of electroplating with silver from a bath of potassium silver cyanide. The operation has been studied by Hittorf[1] among others, who holds that the cation is potassium, and the anion the group $AgCy_2$. Each K ion, as it reaches the cathode, precipitates silver by reacting with the solution in accordance with the equation

$$K + KAgCy_2 = 2KCy + Ag,$$

while the anion $AgCy_2$ dissolves an atom of silver from the anode, and re-forms the complex cyanide $KAgCy_2$ by combining with the 2KCy produced in the reaction described by the above equation. If the anode consists of platinum, cyanogen gas is evolved thereat from the anion $AgCy_2$, and the platinum becomes covered with the insoluble silver cyanide AgCy, which soon stops the current. The coating of silver obtained by the process described above is coherent and homogeneous, while that deposited from a solution of silver nitrate, as the result of the primary action of the current, is crystalline and easily detached.

The corresponding cyanide process in the case of gold is now extensively used for the extraction of gold from its ores. The rock, containing small quantities of gold in a state of very fine division, is treated with potassium cyanide, and the solution of the double cyanide obtained in this way is electrolysed between steel anodes and lead cathodes. Prussian blue, which is again worked up into potassium cyanide, is formed on the anodes, and the gold is removed from the lead cathodes by cupellation.

In the electrolysis of a concentrated solution of sodium acetate, hydrogen is evolved at the cathode and a mixture of ethane and carbon dioxide at the anode. According to Jahn[2],

[1] *Pogg. Ann.* CVI. 517 (1859).

[2] *Grundriss der Elektrochemie*, p. 292 (1895).

the processes at the anode can be represented by the equations

$$2CH_3 . COO + H_2O = 2CH_3 . COOH + O,$$

$$2CH_3 . COOH + O = C_2H_6 + 2CO_2 + H_2O.$$

The hydrogen at the cathode is developed by the secondary action

$$2Na + 2H_2O = 2NaOH + H_2.$$

Many organic compounds can be synthetically prepared by taking advantage of secondary actions at the electrodes, such as reduction by the cathodic hydrogen, or oxidation at the anode[1].

Our knowledge of the nature of the ions has been profitably extended by another method. The changes in the concentration of a solution which occur near the electrodes are in some cases very marked, and it seems necessary to assume that unaltered salt is attached to one of the ions, forming a complex ion. In alcoholic and concentrated aqueous solutions of cadmium iodide, some of the anions appear to be CdI_4 or I_2 (CdI_2), and are perhaps derived from double or Cd_2I_4 molecules[2]. It has even been suggested that molecules of solvent may be attached to ions and be carried along with them under the influence of the electric forces[3].

It is sometimes possible to study the question by examining the conductivity of a solution and its variation with the concentration. The rate of variation with concentration of the equivalent conductivity of an electrolyte (that is, the conductivity divided by the concentration) is much less for salts of monovalent acids than when the valency of the acid is higher. The conductivity curve of potassium permanganate, for example[4], indicates that the acid is monovalent, and the formula of the salt consequently $KMnO_4$.

Again, it is possible to distinguish between double salts and salts of compound acids. Thus Hittorf showed that when a current was passed through a solution of sodium platinichloride,

[1] Lüpke's *Elektrochemie*, Eng. Trans. p. 29.

[2] Hittorf, see below.

[3] W. N. Shaw, *B. A. Report*, 1890, 201; see below, Electric Endosmose.

[4] W. C. D. Whetham, *Phil. Trans.* A, CXCIV. 321 (1900).

the platinum appeared at the anode. The salt must therefore be derived from a compound acid, and have the formula Na_2PtCl_6, the ions being sodium and $PtCl_6$, for if it were a double salt it would decompose as a mixture of sodium chloride and platinum chloride, and both metals would go to the cathode.

Kohlrausch[1] has found that, in the electrolysis of solutions of the salt $PtCl_4 . 5H_2O$, the weight of the cathode remains unaltered for small current densities; he therefore concludes that no platinum is deposited primarily. With greater current densities a grey deposit is obtained, which loses weight on heating and probably contains hydrogen. At the anode oxygen is first evolved, but, as time goes on, it is replaced by chlorine, the solution becoming darker in colour and acquiring a higher conductivity, showing the formation of the acid H_2PtCl_6. Kohlrausch explains the facts by assuming the existence of compound ions of the formula $PtCl_4O$.

Osmond and Houllevigne have studied the electrolysis of solutions of salts of iron, using iron containing carbon for the electrodes. The latter observer has found that, while carbon dissolved in steel is not carried with the current but remains as a muddy deposit at the surface of the anode, combined carbon forms with the iron a complex ion, and is carried with it in the direction of the current[2].

[1] *Wied. Ann.* LXIII. 423 (1897).

[2] *Journ. de Physique*, 3rd series, VII. 708 (1898).

CHAPTER IX.

CONDUCTIVITY OF ELECTROLYTES.

Ohm's law. Experimental methods. Experimental results. Consequences of Ohm's law. Migration of the ions and transport numbers. Mobility of the ions. Experimental measurements of ionic velocity. Influence of concentration. Complex ions. Connexion between the mobility of an ion and its chemical constitution.

Ohm's law.

THE current through a metallic conductor is, to a very great degree of accuracy, proportional to the electromotive force applied. This relation, known as Ohm's law, may be expressed in the form that $C = E/R$, where R is a constant for any given conductor under fixed conditions, and is called its resistance. The law is verified if the resistance is shown to be independent of the current passing through it. The early experimenters, in the course of their investigations, made efforts to discover whether electrolytes also conformed to Ohm's law. It was known that, owing to the reverse force of polarization, no permanent current of moderate intensity could be maintained through an electrolyte unless the electromotive force exceeded a certain limit; but polarization occurs, primarily at any rate, at the electrodes, and it remained to see, when all reverse forces were eliminated, whether the flow of the current in the body of the liquid was in accordance with the law. Eventually F. Kohlrausch, in experiments to be described below, clearly proved that solutions have a real resistance, which remains constant when measured with various currents and by different methods.

The current in a circuit containing an electrolytic cell can therefore be calculated by Ohm's law if from the total electromotive force of the circuit be subtracted the reverse electromotive force due to the polarization of the electrodes and to any changes produced by the current in the nature and concentration of different parts of the solution.

Experimental methods.

Many attempts were made to measure the resistances of electrolytes before a satisfactory method was discovered. Horsford[1] passed a current between two electrodes in a rectangular trough, then moved them nearer together, and determined the resistance of a wire which, when interposed in the circuit, reduced the current to its former value. Assuming that the polarization is equal in the two cases (which, owing to migration, is difficult to insure) the resistance of the wire is the same as that of a column of solution equal in length to the difference of the distances between the electrodes in the two positions. The method was improved by Wiedemann, who used as electrodes plates of the metal present in solution, and thus reduced polarization.

Beetz[2] used an ordinary Wheatstone bridge arrangement, getting rid of nearly all polarization by making his electrodes of amalgamated zinc placed in a neutral solution of zinc sulphate.

Since the electromotive force between any two points of a given circuit is proportional to the resistance between them, the resistance of two parts of a circuit can be compared by comparing the electromotive forces between their ends. In this way Bouty[3] examined many solutions. He placed them in inverted U tubes and passed a current through two of them in series. Tapping electrodes were constructed by putting zinc rods in zinc sulphate solution, with thin siphon tubes, filled with the same solution, to make contact where required. The electromotive forces between the ends of the two tubes were thus compared. The only polarization is at the surfaces of contact of the different solutions.

[1] *Pogg. Ann.* LXX. p. 238 (1847). [2] *Pogg. Ann.* CXVII. p. 1 (1862).
[3] *Ann. de Chemie et de Physique*, 1884, III.

Another way of eliminating the effects of polarization and migration has been used by Stroud and Henderson[1]. Two of the arms of a Wheatstone's bridge are composed of narrow tubes filled with the solution, the tubes being of equal diameter but of different length. The other two arms are equal coils, and metallic resistance is added to the shorter tube till the bridge is balanced. Equal currents then flow through the two tubes; the effects of polarization and migration are the same in each; and the resistance added to the shorter tube must be equal to the resistance of a column of liquid the length of which is the difference in the lengths of the two tubes.

At present the resistance of electrolytes is most frequently determined by means of alternating currents. This method was first successfully adapted to the purpose by Kohlrausch[2], who employed the alternating currents from a small induction coil, and used a telephone as indicator. The electromotive force of polarization in the electrolytic cell is thus rapidly reversed, and never reaches its full magnitude. But, unless proper precautions are taken, a small amount of chemical decomposition can produce so much effect that, even with alternating currents, the polarization is appreciable, and the resistance as measured is found to depend on the rate of alternation. The products of the decomposition of $\frac{1}{70}$ milligram of water on two platinum plates, each having an area of one square metre, will give an electromotive force of about one volt. The electromotive force of polarization is proportional to the surface density of the deposit; its effect can therefore be diminished by increasing the area of the electrodes, a condition obtained by coating them with platinum black. This is done as follows. A current from two accumulators or two or three Daniell cells is passed backwards and forwards between the electrodes through a solution of platinum chloride, which is now usually prepared by dissolving 1 part of platinum chloride (i.e. H_2PtCl_6) and 0·008 part of lead acetate in 30 parts of water.

[1] *Phil. Mag.* [5] XLIII. 19 (1897); *Proc. Phys. Soc. Lond.* XV. 13 (1897).

[2] *Pogg. Ann.* CXXXVIII.—CLIII. (1869—1874); *Wied. Ann.* VI.—LXIV. (1877—1898); also Kohlrausch und Holborn, *Leitvermögen der Elektrolyte*, Leipzig, 1898.

The strength of the current is adjusted to give a moderate evolution of gas. The platinized plates obtained by this method have very large effective surfaces, and are quite satisfactory for the examination of strong solutions. They have the power, however, of absorbing a certain amount of salt from the solutions and of giving some of it up again when water or a more dilute solution is placed in the cell. The investigation of very dilute solutions, hereby made difficult, has been successfully carried out by first platinizing the electrodes and then heating them to redness. This process gives a gray surface which has enough area to prevent polarization from interfering with the results, while it does not absorb any appreciable quantity of salt[1]. Various causes of disturbance must be taken into account or eliminated by adjustment of the arrangements; both the self-induction of the circuit[2] and its electrostatic capacity[3] may become appreciable.

The most usual arrangement of apparatus is shown diagrammatically in Fig. 47. The metre bridge is adjusted till no

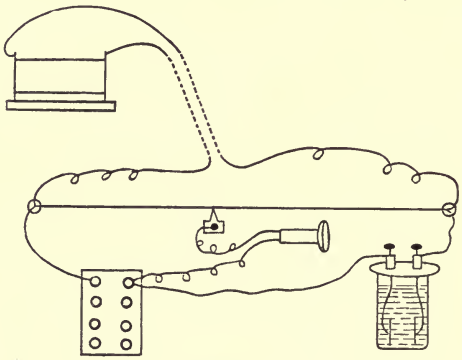


Fig. 47.

sound is heard in the telephone, when the well-known relation between the resistances of the four arms of the bridge holds good.

[1] Whetham, *Phil. Trans.* A, CXCIV. 329 (1900).

[2] *Encycl. Brit.*, Art. Electricity, or *B.A. Report*, 1886, 384.

[3] Chaperon, *Compt. Rend.* CVIII. 799 (1889), and Kohlrausch, *Zeits. phys. Chem.* XV. 126 (1894).

The telephone is not a very pleasant instrument to use in this way, and a modification of the method, used by MacGregor[1], Fitzpatrick[2] and the present writer[3], is more rapid and also more accurate. The current from one or more dry cells is led to an ebonite drum, turned by a hand-wheel and cord, on which are fixed brass strips with wire brushes touching them in such a manner that the current is reversed several times in each revolution. The wires from the drum are connected with an ordinary resistance box in the same way as the battery wires of the usual Wheatstone's bridge. A moving coil galvanometer is used as indicator, and on the other end of the drum there is another set of strips, arranged to periodically reverse the connexions of the galvanometer, so that any residual current which flows through it is direct and not alternating. These strips are rather narrower than the first set, and thus the galvanometer circuit is made just after the battery circuit is made and broken just before the battery circuit is broken. The high moment of inertia of the galvanometer coil makes its period of swing very slow compared with the period of alternation of the current, and therefore the slight residual effects of polarization and other periodic disturbances are prevented from sensibly affecting the galvanometer. When the measured resistance is not altered by increasing the speed of the commutator, or changing the ratio of the arms of the bridge, the disturbing effects may be considered to be eliminated.

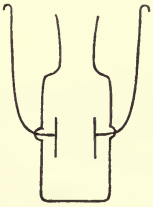


Fig. 48.

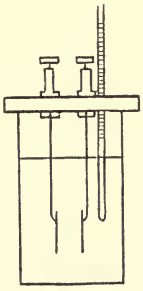


Fig. 49.

[1] *Trans. Roy. Soc. Canada*, 1882, 21.
[2] *B.A. Report*, 1886, p. 328.
[3] *Phil. Trans.* A, CXCIV. 330 (1900).

The form of vessel chosen to contain the electrolyte depends on the order of resistance to be measured. For dilute solutions the shapes of figures 48 and 49 will be found convenient, while for more concentrated solutions, those indicated in figures 50 and 51 are suitable.

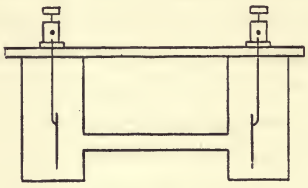


Fig. 50.

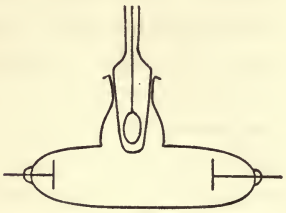


Fig. 51.

The absolute resistances of certain solutions have been determined by Kohlrausch by comparison with mercury, and by using one of these solutions in any cell, the constant of that cell can be found once for all. From the observed resistance of any given solution in the cell, the resistance of a centimetre cube, or the specific resistance, can then be calculated. The reciprocal of this, or the conductivity, is a more generally useful constant; it is conveniently expressed in terms of a unit equal to the reciprocal of an ohm. This unit is sometimes written as a "mho," a name it is not intended to use in this book.

As the temperature coefficient of conductivity is large, usually about two per cent. per degree, it is necessary to place the resistance cell in a paraffin or water bath, and observe its temperature with some accuracy.

Experimental results.

Kohlrausch expresses his results in terms of equivalent conductivity, that is the conductivity k divided by the number of gram-equivalents of electrolyte per litre n. He finds that, as the concentration of solutions of monovalent salts, such as potassium chloride, sodium nitrate, etc., diminishes, the value of k/n approaches a limit, and, if the dilution is carried far enough, becomes constant, that is to say, at great dilution the conductivity is proportional to the concentration. In establishing this result, Kohlrausch used very pure

UNIVERSITY OF CALIFORNIA

water prepared by careful distillation. He observed that the resistance of the water continually increased as the process of purification proceeded. The conductivity of the water, and of the slight impurities which must always remain, was subtracted from that of the solution, and the result, divided by n, gave the equivalent conductivity of the substance dissolved. This method of calculation appears justifiable, for, as long as conductivity is proportional to concentration, it is evident that each part of the dissolved matter produces its own independent effect, so that the total conductivity is the sum of those of the parts, and when this relation ceases to hold, the conductivity of the solution has, in general, become so great that the part due to the solvent is negligible.

The general result of these experiments can be graphically represented by plotting k/n as ordinates, and $n^{\frac{1}{3}}$ as abscissae; $n^{\frac{1}{3}}$ is a number proportional to the reciprocal of the average distance between the molecules, to which it seems likely that the equivalent conductivity will be closely related. The general forms of the curves for the neutral salt of a monovalent acid and for a caustic alkali or monovalent acid (like HCl) are shown in Fig. 52. The curve for the neutral salt comes to a limiting value, while that for the acid or alkali attains a maximum at a certain very small concentration, and falls again when the

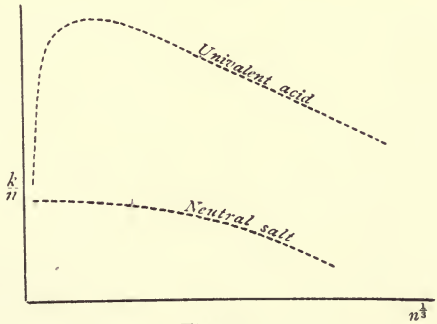


Fig. 52.

dilution is pushed to extreme limits. This fall has usually been considered to be due to chemical action between the acid and

the residual impurities in the water, which, at such great dilution, are present in quantities quite comparable with the amount of acid. The phenomena however seem too regular to be due to the action of such impurities, for the fall begins at about the same dilution whatever the amount of impurity present. An explanation is suggested if we consider that the cases in which the fall occurs are those in which one of the ions (H or OH) of the solute is present in the solvent water[1]. Whatever be the cause of the phenomena we must take the maximum value of the equivalent conductivity to be the limit in the case of acids though it is possible that this method may give too low a result.

It will be seen from the tables in the appendix that the values of the equivalent conductivities of all neutral salts are, at great dilution, of the same order of magnitude, while those of acids at the maximum are about three times as great.

Passing to salts of divalent acids and other more complicated electrolytes, Kohlrausch found it impossible to reach such definite limiting values for the equivalent conductivity as were given by monovalent salts. Moreover, the influence of increasing concentration was more marked, the curves sloping at much larger angles. These changes in the phenomena were still greater when, as in copper sulphate, both metal and acid were divalent, and greatest of all in such substances as ammonia and acetic acid, which have very small conductivities when dissolved in water. We shall presently return to this subject.

One of the most important results of Kohlrausch's work consisted in the proof that the resistance of a given electrolyte had a definite value, which was independent of the particular method used to determine it. This amounts to a demonstration of Ohm's law within the limits of the conditions of the experiments. A more direct proof of the law for strong currents was given by FitzGerald and Trouton[2], who showed that the measured resistance was independent of the strength of the current.

[1] Whetham, *Phil. Trans.* A, CXCIV. 353 (1900).

[2] *B. A. Report*, 1886, p. 312.

Consequences of Ohm's law.

The conformity of electrolytes with Ohm's law is most instructive. Since any electromotive force, however small, is able to produce a corresponding current, there can be no appreciable reverse electromotive forces in the interior of an electrolyte, and no measurable amount of chemical work can be there done by the current. It follows either that the function of the current is merely directive, controlling the direction of the motions of the ions which it already finds in a state of mobility, or else that the work done in splitting up one molecule is exactly equal to that given back in the formation of the next.

The first of these hypotheses was advanced by Clausius[1] to explain electrolysis, and, as it is the one generally adopted, we will examine the evidence for it in some detail. If two solutions containing the salts AB and CD are mixed, double decomposition is found to occur—AD and CB being formed, till a certain part of the first pair of substances has been transformed into an equivalent amount of the second pair. The proportions between the four salts AB, CD, AD and CB, which finally exist in solution, are the same under similar conditions of temperature and pressure whether we begin with AB and CD or with AD and CB. The phenomena were found by Guldberg and Waage to be fully represented by a theory which supposed that both the change from AB and CD into AD and CB, and the reverse change from AD and CB to AB and CD were always going on, and that the quantities transformed per second were proportional to the product of the active masses of the original substances and to a coefficient k, depending on the temperature and pressure, which expresses the rate at which the action proceeds when the active masses of the reagents are each unity, and measures the affinity producing the reaction. If the active masses of AB, CD, AD, CB are p, q, p', q' respectively, and k and k' the two coefficients of affinity, we get for the rate of transformation of AB and CD into AD and CB

$$kpq,$$

and for the velocity of the reverse change

$$k'p'q'.$$

[1] *Pogg. Ann.* CI. p. 338 (1857).

When there is equilibrium, these two rates of transformation must be equal and opposite, and we get

$$kpq = k'p'q' \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (27).$$

This equation can, as we shall see later, be obtained for dilute solutions by the principles of thermodynamics, and its results have been experimentally confirmed for many cases. It may, however, be explained as above, by a kinetic theory of the phenomena, and this view of double decomposition is universally admitted to be a true one. But in order that this process of chemical change in opposite directions should continually go on, it is necessary to have perfect freedom of interchange between the parts of the molecules, and to imagine that separations and reunions are perpetually occurring among them. This hypothesis was first advanced from the chemical side by Williamson[1] in order to explain the process of etherification.

A study of chemical changes shows that it is always the electrolytic ions of a salt that are concerned in the reactions. The tests for a salt, potassium nitrate for example, are the tests not for KNO_3, but for its ions K and NO_3, and in cases of double decomposition, it is always these ions that are exchanged. If an element is present in a compound otherwise than as an ion, it is not interchangeable, and cannot be recognized by the usual tests. Thus neither the chlorates, which contain the ion ClO_3, nor monochloracetic acid, show the reactions of chlorine; and the sulphates do not answer to the tests which indicate the presence of sulphur as sulphide.

It seems certain, then, that the parts of the molecules in solution are continually interchanging, that the electrolytic ions are also the parts which enter into chemical combinations, and that the effect of a current is merely so to control the direction of these decompositions and recompositions, that, on the whole, a stream of positively electrified ions travels in one direction, and a stream of negatively electrified ions in the other. As far as we have gone, there is no evidence to show that the ions remain dissociated for any appreciable time, and

[1] *Chem. Soc. Journal*, IV. 110 (1852).

the reasoning given above merely proves that there is freedom of interchange. This freedom may only exist in the case of those molecules which, according to the kinetic theory, at any instant happen to be moving with a velocity so much greater than the average, that, on colliding with another molecule, they produce sufficient impact to cause dissociation, and make rearrangement possible. So much seems to follow from the truth expressed in Ohm's law and the phenomena of chemical action. There is, however, further evidence, which we shall discuss later, that the ions remain dissociated, or at all events keep a certain amount of freedom, throughout a considerable fractional part of their existence.

The migration of the ions and transport numbers.

Kohlrausch's work on solutions of simple salts of monovalent acids also drew attention to the additive nature of their conductivity. The equivalent conductivity in such cases can be represented as the sum of two independent quantities, one depending solely on the anion, and the other on the cation. To examine the meaning of this result, we must remember that, as we saw in the last chapter, the experimental relations summarized in Faraday's laws indicate that electrolysis is to be considered as a process resembling convection, a constant stream of cations moving with the current, and a stream of anions in the opposite direction. The quantity of electricity thus conveyed will be proportional to the number of carriers and to the speed with which they travel.

If we pass a current between copper plates through a solution of copper sulphate, the colour of the liquid in the neighbourhood of the anode becomes deeper, and in the neighbourhood of the cathode lighter in shade. This is well seen if the electrodes are arranged horizontally with the anode underneath. When the electrodes are of copper, the quantity of metal in solution remains constant, since it is dissolved from the anode as fast as it is deposited at the cathode, but if we use platinum electrodes, the amount in solution becomes continually less, since more salt is taken from the neighbourhood of the cathode than from the anode, and the colour of

the solution, therefore, becomes pale more rapidly near the cathode than near the anode.

This subject was first systematically investigated by Hittorf[1], who examined many solutions in a manner which enabled the liquid round the two electrodes to be separately analysed after the passage of the current.

Two explanations of these changes in concentration seem possible. It may be that the ions are really complex, unaltered salt being attached to the anion or solvent to the cation, so that some of the anions have the composition $\overset{+}{Cu}(CuSO_4)$ or some of the cations the composition $\overset{-}{SO_4}(H_2O)$; in this way salt would be drawn to the anode or solvent to the cathode. It may be that the velocities of the ions are different, the anion, in the case of copper sulphate, travelling faster than the cation. It is possible that, in many cases, both these effects occur; and indeed, as we shall see later, the evidence indicates that such is the case. In developing the hypothesis of different ionic velocities it is certain that if the opposite ions move with equal velocities, the result of the passage of the current will be that, while the composition of the middle portion of the solution remains unaltered, the products of the decomposition, which appear at the electrodes, are taken in equal proportions from the solution surrounding the anode, and from that round the cathode. If, however, one of the ions travels faster than the other, it will get away from the portion of the solution whence it comes more quickly than the other ion enters. When the electrodes are of non-dissolvable material, therefore, the concentration of the liquid in this region will fall faster than in that round the other electrode.

Let us assume that the cation drifts to the right with a velocity u, and the anion to the left with a velocity v. The velocity of the cation can be resolved into $\frac{1}{2}(u+v)$ and $\frac{1}{2}(u-v)$, and the velocity of the anion into $\frac{1}{2}(v+u)$ and $\frac{1}{2}(v-u)$. On pairing these components, we have a drift of the two ions right and left, each with a speed $\frac{1}{2}(u+v)$, involving no accumulation

[1] *Pogg. Ann.*, LXXXIX. 177, XCVIII. 1, CIII. 1, CVI. 337, 513 (1853–9).

at the electrodes, and a uniform flow of the electrolyte itself without separation with a speed $\frac{1}{2}(u-v)$ to the right[1].

Thus at the cathode there is a gain of electrolyte equal to $\frac{1}{2}(u-v)$, and a loss, due to electrolytic separation, of $\frac{1}{2}(u+v)$: a total loss of v. At the anode there is a loss of $\frac{1}{2}(u-v)$ and a loss of $\frac{1}{2}(u+v)$, a total loss of u. The initial losses of electrolyte at the two electrodes, then, before diffusion sensibly affects the result, are in the same ratio as the velocities of the ions travelling away from them.

The process can be clearly illustrated by a method due to

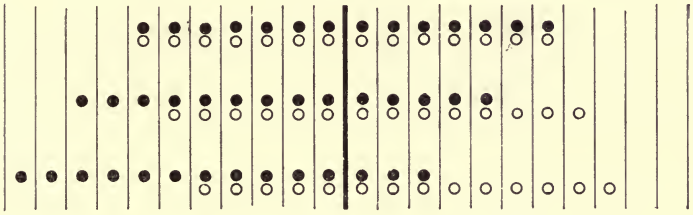


Fig. 53.

Hittorf. In Fig. 53 the black dots represent the one ion, and the white circles the other. If the black ions move to the left twice as fast as the white ions move to the right, the black ions will move over two of our spaces while the white ones move over one. Two of these steps are represented in the diagram. At the end of the process it will be found that six molecules have been decomposed, six black ions being liberated at the left and six white ions at the right. Looking at the combined molecules, however, we see that while five remain on the left side of the middle line, only three are still present on the right. The left-hand side, towards which the faster ions moved, has lost two combined molecules, while the right-hand side, towards which the slower ions travelled, has lost four—just twice as many. Thus we see that the ratio of the masses of salt lost by the two sides is the same as the ratio of the velocities of the ions leaving them. Therefore, on the assumption that no complex ions are present, by analysing

[1] Larmor, *Aether and Matter*, Cambridge, 1900, p. 290.

the contents of a solution after a current has passed, we can calculate the ratio of the velocities of its two ions. A long series of measurements of this kind has been made by Hittorf[1], Kuschel[2], Lenz[3], Loeb and Nernst[4], Bein[5], Hopfgartner[6], Kümmel[7], Kistiakowsky[8] and others, who used various forms of apparatus arranged so as to enable the anode and cathode solutions to be separately examined after the passage of the current. One such

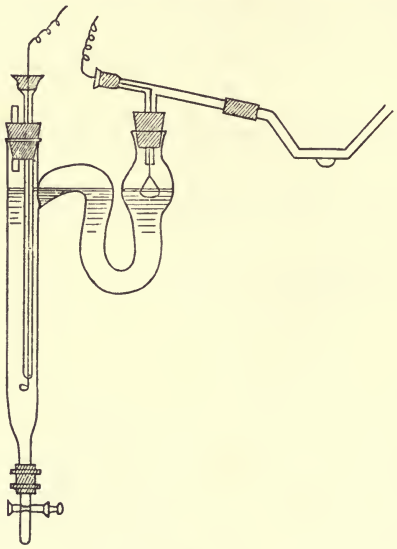


Fig. 54.

apparatus used by Bein is shown in Fig. 54. Hittorf called the phenomenon the "migration of the ions," and expressed his results in terms of a transport number, or migration constant, which gives the amount of salt taken from the neighbourhood of one electrode as a fraction of the whole amount that disappears. If there are no complex ions, it also expresses the ratio of the

[1] *loc. cit.* p. 208.
[2] *Wied. Ann.* XIII. 289 (1881).
[3] *Mém. Pétersb. Acad.* IX. 30 (1882).
[4] *Zeits. f. physikal. Chemie,* II. p. 948 (1883).
[5] *Wied. Ann.* XLVI. 29 (1892) and *Zeits. phys. Chem.* XXVII. 1 (1898).
[6] *Zeits. phys. Chem.* XXV. 115 (1898).
[7] *Wied. Ann.* LXIV. 665 (1898).
[8] *Zeits. phys. Chem.* VI. 97 (1890).

velocity of one ion to the sum of the opposite ionic velocities. Many results on the subject were collected by T. C. Fitzpatrick in his tables of "The Electro-Chemical Properties of Aqueous Solutions," published in the *British Association Report* for 1893, and reprinted by permission in the appendix to this book. A more recent list appeared in Kohlrausch and Holborn's book *Das Leitvermögen der Elektrolyte*[1], from which is taken the table on the next page. In it results in *italics* are considered by Kohlrausch to have been obtained under uncertain conditions. The numbers represent the migration constants for the anions. Thus $CuSO_4$ ·632 means that the amount of salt taken from the cathode vessel is to the whole amount decomposed as ·632 : 1, and is therefore to the amount taken from the anode vessel as ·632 : ·368. The concentration n gives the number of gram equivalents of salt per litre of solution.

The transport numbers for cadmium iodide, which, for solutions of more than half normal concentration, are greater than unity, show that the cathode vessel loses more salt than the whole solution does. It follows that some unaltered salt must travel through the solution towards the anode, and this result at once led to the conception of complex ions of the type I (CdI_2). The changes with concentration in the transport numbers of many other substances, such as calcium chloride and copper sulphate, seem too great to be explained by a different rate of variation for the two ions of the quasi-frictional resistance which the solution offers to their passage, and suggest that complex ions may exist in many solutions. Other evidence in favour of this supposition will be given later.

Bein has shown that, if a membrane be used to separate the anode and cathode solutions, a considerable effect, varying with the nature of the membrane, is produced on the transport numbers.

Mobility of the ions.

A further step was taken in the year 1879 by Kohlrausch[2], who showed that a knowledge of the conductivity of a solution enabled the sum of the opposite ionic velocities to be calculated. We have seen that

[1] Leipzig, 1898.

[2] *Wied. Ann.* vol. VI. p. 160 (1879).

Transport Numbers.

$n=$ / $V=1/n=$	0·01 / 100	0·02 / 50	0·05 / 20	0·1 / 10	0·2 / 5	0·5 / 2	1 / 1	1·5 / ·67	2 / ·5	3 / ·33	5 / ·20	7 / ·14	10 / ·10
K{Cl, Br, I}	0·506	·507	·507	·508	·509	·513	·514	·515	·515	*·516*	—	—	—
NH_4Cl	—	—	·614	·617	·620	·626	·637	*·640*	*·642*	·646	*·650*	—	—
NaCl	0·63	·65	·67	·69	·71	·73	·739	·741	·745	·752	·763	·774	—
LiCl	—	—	—	·497	·496	·492	·487	·482	·479	—	—	—	—
KNO_3	—	—	—	·615	·614	·612	*·611*	*·610*	*·608*	·603	·585	—	—
$NaNO_3$	0·528	·528	·528	·528	·527	·519	·501	·487	·476	—	—	—	—
$AgNO_3$	—	—	—	·33	·33	·33	*·331*	*·332*	*·332*	*·333*	·335	—	—
$KC_2H_3O_2$	—	—	—	*·44*	*·43*	*·43*	*·425*	·422	·421	·417	—	—	—
$NaC_2H_3O_2$													
KOH	—	—	—	·735	·736	*·738*	*·740*	—	—	—	—	—	—
NaOH	—	—	*·81*	*·82*	*·82*	*·82*	·825	—	—	—	—	—	—
LiOH	—	—	—	*·85*	·85	·861	*·873*	·890	—	—	—	—	—
HCl	—	—	·172	·172	·172	·173	·176	*·180*	*·185*	·200	*·238*	·292	—
$\frac{1}{2}BaCl_2$	*0·56*	*·565*	*·575*	*·585*	*·595*	*·615*	·640	·650	·657	—	—	—	—
$\frac{1}{2}CaCl_2$	*0·58*	*·59*	*·61*	*·64*	*·66*	*·675*	·686	·695	*·700*	·710	·737	·764	·790
$\frac{1}{2}MgCl_2$	—	—	*·63*	*·66*	·68	·69	·709	*·718*	*·729*	*·747*	·776	·799	—
$\frac{1}{2}CdCl_2$	*0·57*	*·58*	*·59*	*·62*	*·65*	*·69*	*·72*	·73	·745	·767	·865	·995	—
$\frac{1}{2}CdI_2$	0·56	·59	·64	*·71*	*·83*	*1·00*	1·12	1·18	1·22	1·25 to 2·5		—	—
$\frac{1}{2}K_2CO_3$	—	—	*·39*	*·40*	*·41*	·435	·434	·421	·413	·404	*·380*	*·355*	—
$\frac{1}{2}Na_2CO_3$	—	—	*·52*	*·53*	*·53*	*·54*	·548	*·546*	*·542*	*·530*	—	—	—
$\frac{1}{2}MgSO_4$	—	—	*·60*	*·64*	*·66*	*·70*	·74	·75	*·76*	·760	—	—	—
$\frac{1}{2}CuSO_4$	—	·62	·626	·632	·643	·668	·696	·714	·720	—	—	—	—
$\frac{1}{2}H_2SO_4$	—	—	*·193*	*·191*	*·188*	·182	·174	*·169*	*·168*	·170	*·190*	*·216*	·268

we can represent the facts by considering the process of electrolysis to be a kind of convection, the ions moving through the solution and carrying their charges with them. Each monovalent ion may be supposed to carry a certain definite charge, which we can take to be the ultimate indivisible unit of electricity; each divalent ion carries twice that amount, and so on.

Let us consider, as an example, the case of an aqueous solution of potassium chloride of which the concentration is m gram-equivalents per cubic centimetre. There will then be m gram-equivalents of potassium ions and the same number of chlorine ions in this volume. Let us suppose that on each gram-equivalent of potassium there reside $+q$ units of electricity, and on each gram-equivalent of chlorine ions $-q$ units. If u denote the average velocity of the potassium ions, the positive charge carried per second across unit area normal to the flow is mqu. Similarly, if v be the average velocity of the chlorine ions, the negative charge carried in the opposite direction is mqv. But positive electricity moving in one direction is equivalent to negative electricity moving in the other, so that the total current, C, is $mq(u+v)$.

Now let us consider the amounts of potassium and chlorine liberated at the electrodes by this current. At the cathode, if the chlorine ions were at rest, the excess of potassium ions would be the number arriving in one second, viz. mu. But, since the chlorine ions move also, a further separation occurs, and mv potassium ions are left without partners. The total number of gram-equivalents liberated is therefore $m(u+v)$. Now, by Faraday's law, the liberation of one gram-equivalent of any ion involves the passage of a definite quantity Q of electricity round the circuit. Thus, in one second, the total quantity passing, that is the current, is $mQ(u+v)$. On comparing this result with the first expression for the same current, it follows that the charge, q, on one gram-equivalent of either ion is equal to the quantity of electricity passing round the circuit when the gram-equivalent is liberated.

We know that Ohm's law holds good for electrolytes, so that the current C is also given by $-kdP/dx$, where k denotes

the conductivity of the solution, and $-dP/dx$ the potential gradient, i.e. the fall in potential per unit length along the lines of current flow.

Thus $$mq(u+v) = -k\frac{dP}{dx};$$

or $$u+v = -\frac{k}{mq}\cdot\frac{dP}{dx} \quad \text{.....(37),}$$

an equation in which everything may be expressed in centimetre-gram-second units. By measuring $1/k$ in ohms (an ohm being 10^9 C.G.S. units), q in coulombs (10^{-1}), and writing n for the number of gram-equivalents of solute per litre instead of per cubic centimetre, we get

$$u+v = -10^{-5}\frac{k}{nq}\cdot\frac{dP}{dx}.$$

Now q is 96440 coulombs (p. 188), so that for a potential gradient of one volt per centimetre (10^8 C.G.S. units), we have

$$u_1+v_1 = 1{\cdot}037\times10^{-2}\times\frac{k}{n} \quad \text{.....(38),}$$

which gives the relative velocity (or the sum of the opposite velocities) of the two ions in centimetres per second under unit potential gradient. These numbers, u_1 and v_1, measure what we may call the mobilities of the two ions.

Since the transport numbers give us the ratio of the ionic velocities if no complex ions are present, we can deduce the absolute values of u_1 and v_1 from this theory. Thus, for instance, the conductivity of a solution of potassium chloride containing one-tenth of a gram-equivalent per litre is 0·01119 reciprocal ohms at 18° C. Therefore

$$u_1+v_1 = 1{\cdot}037\times10^{-2}\times0{\cdot}1119$$
$$= 0{\cdot}001165 \text{ cm. per sec.}$$

Hittorf's experiments show us that the ratio of the velocity of the anion to that of the cation in this solution is ·51 : ·49. The absolute velocity of the chlorine ion under unit potential gradient is therefore 0·000595 cm. per sec., and that of the potassium ion 0·000570 cm. per sec. Similar calculations can be made for solutions of other concentrations. The following table gives the ionic mobilities of three chlorides of alkali

metals as multiples of 10^{-6} cm. per sec., per volt per cm. at 18° C.

n	KCl			NaCl			LiCl		
	u_1+v_1	u_1	v_1	u_1+v_1	u_1	v_1	u_1+v_1	u_1	v_1
0	1363	667	697	1151	454	697	1060	364	697
0·0001	1348	661	688	1140	452	688	1047	360	688
·001	1326	650	677	1121	444	677	1023	346	677
·01	1276	625	650	1070	419	650	971	321	650
·03	1230	603	627	1023	394	629	926	301	625
·1	1165	570	595	961	364	598	862	262	600
·3	1099	536	563	885	327	558	782	219	563
1·0	1021	496	525	773	281	492	658	171	487
3·0	920	446	474	588	208	380	468	116	351
5·0	—	—	—	442	155	288	337	81	257
10·0	—	—	—	—	—	—	118	25	93

These numbers clearly show the increase in ionic mobility as the dilution gets greater. Moreover, if we compare the values for the chlorine ion obtained from observations on these three different salts, we see that, as the solutions get very weak, the mobility of the chlorine ion becomes the same in all of them. Similar phenomena appear in other cases of simple monovalent salts; and, in general, we may say that, at great dilution, the velocity of an ion in the solution of such a salt is independent of the nature of the other ion present. From this result we may deduce the existence of specific ionic mobilities, the values of which are given in the following table for different monovalent ions in centimetres per second per volt per centimetre.

K	67×10^{-5}	Cl	70×10^{-5}
Na	45 „	I	70 „
Li	36 „	NO_3	65 „
NH_4	67 „	OH	184 „
H	323 „	$C_2H_3O_2$	36 „
Ag	58 „	$C_3H_5O_2$	33 „

Having once obtained these numbers, we can calculate the equivalent conductivity of the dilute solution of any salt containing the ions referred to, and the comparison of such values

with observation furnished the first confirmation of Kohlrausch's theory. Some exceptions, however, are known. Thus, acetic acid and ammonia give solutions of much lower conductivity than is indicated by the sum of the specific mobilities of their ions as determined from other compounds.

Experimental measurements of ionic velocity.

Oliver Lodge was the first to directly measure the velocity of transport of an ion[1]. In a horizontal glass tube connecting two vessels filled with dilute sulphuric acid, he placed a solution of sodium chloride in solid agar-agar jelly. This solid solution was made alkaline with a trace of caustic soda to bring out the red colour of a little phenol-phthalein added as indicator. A current was then passed from one vessel to the other along the tube. The hydrogen ions from the anode vessel of acid were thus carried along the tube, and decolorized the phenol-phthalein as they travelled. By this method the velocity of the hydrogen ion through a jelly solution under a known potential gradient could be observed. The results of three experiments gave 0·0029, 0·0026, and 0·0024 cm. per sec. as the velocity of the hydrogen ion for a potential gradient of one volt per centimetre. Kohlrausch's number is 0·0032 for the dilution corresponding to maximum conductivity. Lodge does not mention the concentration of his solution, but it was probably large enough to appreciably reduce the velocity. Experiments in which the motion of other ions was traced by the formation of precipitates, gave results differing considerably from the theoretical numbers, probably owing to the indeterminate values of the potential gradient.

When the current density at the cathode in a solution of copper sulphate exceeds a certain limit, copper is deposited as a brown or black hydride. C. L. Weber[2] attributed this to the inability of the copper ions to migrate fast enough to keep up the supply for carrying the current, part of which will consequently be conveyed by sulphuric acid formed by the action of SO_4 ions on the water. By measuring the limiting

[1] *British Association Report*, 1886, p. 389.

[2] *Zeits. phys. Chem.* IV. 182 (1889).

current density and the conductivity of the solution, he estimated the speed of the copper ions when they could travel just fast enough to carry all the current, and hence he deduced their specific velocity. Similar methods were used for solutions of cadmium sulphate and zinc nitrate. The copper sulphate measurements were repeated with an improved apparatus by Sheldon and Downing[1]. This method does not appear to be a very good one, for the dilution of the liquid round the cathode makes it impossible to accurately determine the conductivity of the solution concerned. This source of error will make the deduced velocities too great.

The velocities of a few other ions have been directly determined in another way by the present writer[2]. Two solutions, having one ion in common, of equivalent concentrations, different densities, different colours, and nearly equal specific resistances, were placed one over the other in a vertical glass tube. In one case, for example, decinormal solutions of potassium carbonate and potassium bichromate were used. The colour of the latter is due to the presence of the bichromate group, Cr_2O_7. When a current was passed across the junction, the anions CO_3 and Cr_2O_7 travelled in the direction opposite to that of the current, and their velocity could be determined by measuring the rate at which the colour boundary moved. Similar experiments were made with alcoholic solutions of cobalt salts, in which the mobility of the ions was found to be much less than in water. The behaviour of agar jelly was then investigated, and the mobility of an ion was shown to be very little less in a solid jelly than in an ordinary liquid solution. The velocities could therefore be measured by tracing the change in colour of an indicator or the formation of a precipitate. Thus decinormal jelly solutions of barium chloride

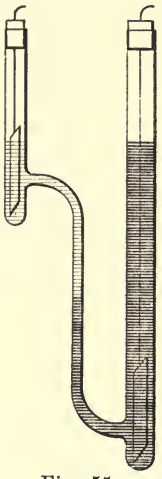


Fig. 55.

[1] *Physical Review*; I. 51 (1893).

[2] *Phil. Trans.* A, CLXXXIV. 337 (1893); *Phil. Mag.* Oct. 1894; *Phil. Trans.* A, CLXXXVI. 507 (1895).

and sodium chloride, the latter containing a trace of sodium sulphate, were placed in contact. Under the influence of an electromotive force, the barium ions moved up the tube, and their presence was shown by the trace of insoluble barium sulphate formed. By keeping the conductivities of the two solutions nearly the same, discontinuity of potential gradient was avoided, and the gradient could then be calculated from the area of cross section of the tube, the conductivity of the solution, and the strength of the current as measured in a galvanometer.

In dilute aqueous solutions of simple salts, the direction of motion observed at the junctions was always normal; but as the concentration was increased, in some cases, such as that of alcoholic cobalt solutions, more than one boundary line appeared, and the direction of some of these lines was occasionally even reversed. In order to explain these results it seems necessary to assume the existence of complex ions, unaltered salt being attached to one or other of the simple ions.

The following table shows the velocities of the ions which have been experimentally determined by the methods of Lodge and Whetham. A comparison is given with their values as calculated, for the same concentration, on Kohlrausch's theory.

Name of Ion	Concentration of solution in gram-equivalents per litre	Specific ionic velocity in centimetres per second	
		Calculated from Kohlrausch's theory	Observed
Hydrogen in chlorides	—	0·0028	0·0026
,, in acetates	0·07	0·000048	0·000065
Copper (in chlorides)	0·1	—	0·00031
Barium	0·1	0·00037	0·00039
Calcium	0·1	0·00029	0·00035
Silver	0·1	0·00046	0·00049
Sulphate group (SO_4)	0·1	0·00049	0·00045
Bichromate group (Cr_2O_7) ...	0·1	0·00047	0·00047
Cobalt (in alcoholic $CoCl_2$) ...	0·5	—	0·000022
,, (,, ,, $Co(NO_3)_2$)	0·05	—	0·000044
Chlorine (in alcoholic $CoCl_2$)	0·05	—	0·000026
Nitrate group (NO_3) (in alcoholic $Co(NO_3)_2$)	0·05	—	0·000035

NOTE.—The migration data for solutions of copper chloride are not known. The specific ionic velocity of copper at infinite dilution (when it would be independent of the nature of the combination) is given by Kohlrausch as 0·00031, but in a solution of the strength used it would be considerably less. The sum of the ionic velocities of cobalt chloride in alcohol, as calculated from the conductivity, is 0·000060 cm. per sec., and that of cobalt nitrate 0·000079. These numbers are to be compared with the sum of the observed velocities given in the table—namely, 0·000048 and 0·000079 respectively.

These experiments, it will be noticed, depend on the phenomena which occur at the junction of two solutions when a current is passed across it. It was observed by Gore[1] that in such a case the surface of contact sometimes remained clear, giving a sharp boundary, and sometimes became blurred and indistinct. Similar results were obtained in the experiments under consideration, and shown by the writer to depend on the relative conductivities of the two solutions. The electromotive force between two points of a circuit is proportional to the resistance, as Ohm's law indicates, and the potential gradients in the two solutions are proportional to their specific resistances. Since one ion, let us say the anion, is the same in each solution, a solution of high resistance means one in which the cation has a low velocity, and a solution of low resistance contains a fast moving cation. Now, if the current pass from the liquid of high to that of low resistance, a cation which chances to get in front of the boundary will find itself in a region of lower potential gradient, and will, therefore, drop back again into line, and if one of the faster ions find itself behind the boundary, it will have entered a region of higher potential gradient and will be once more pushed forwards. The boundary therefore keeps sharp and distinct while moving with the current. On the other hand, if the current flow from the low resisting to the high resisting liquid, a straggling slow ion will drop behind into a region of smaller potential gradient, and be still further retarded, while a wandering fast ion will enter a region where the higher electric forces will still further hasten it. The boundary will therefore become blurred and indistinct. Thus the condition necessary for the existence and

[1] *Proc. R. S.* 1880 and 1881.

permanence of a sharp boundary is, that a specifically slower ion must follow a specifically faster ion. The general theory of such boundaries has been considered by Kohlrausch[1] and H. Weber[2].

Orme Masson has applied these results to obtain a more accurate method of experimentally determining ionic velocities[3]. From what has been said, it follows that a current passing from a solution of high to a solution of low resistance, adjusts the potential gradients so that the actual velocity of the specifically slow ion in the region of high potential gradient is equal to that of the fast ion in the region of low potential gradient. Masson placed a jelly solution of a colourless salt, potassium chloride for instance, in the central region of a horizontal glass tube, the ends of which were filled with jelly solutions of salts, one with a coloured anion and one with a coloured cation, these ions being specifically slower than the ions of the potassium chloride which they respectively adjoined. The solutions used for this purpose were potassium chromate with a yellow anion, and copper sulphate with a blue cation. The chromate ion and the copper are slower than chlorine and potassium respectively, and thus, if a current be passed from the copper end through the chloride to the chromate, at each end a specifically slower follows a faster ion, and the condition of stability of the boundary is fulfilled. The potential gradient is the same throughout the chloride solution, and can be calculated from the conductivity and the current strength, and therefore the speed of the colour boundaries at each end gives the velocity of potassium and chlorine under the same potential gradient. By measuring the relative velocity of these two margins, therefore, the ratio between the velocities of potassium and chlorine can be determined, and compared with Hittorf's migration constant. Other salts were examined in the same way, and the relative mobilities of different ions, thus measured, were found to agree well with Kohlrausch's values.

[1] *Wied. Ann.* LXII. 209 (1897).
[2] *Sitz. Akad. Wiss. Berlin*, 936 (1897).
[3] *Phil. Trans.* A, CXCII. 331 (1899).

The following table gives the mobilities of the ions, relatively to the value for potassium, which is put equal to 100, as determined by Masson, Kohlrausch's theoretical values for one-tenth normal solutions being appended for comparison.

	Chlorides			Sulphates			Kohlrausch
	$n = \cdot 5$	$n = 1$	$n = 2$	$n = \cdot 5$	$n = 1$	$n = 2$	$n = \cdot 1$
K	100	100	100	100	100	—	100
Na	65·7	65·4	65·8	66·9	66·9	—	62
Li	44·7	45·2	—	47·1	44·4	45·2	46
NH_4	—	100	—	—	—	—	96
$\frac{1}{2}Mg$	—	—	—	40·5	36·9	38·7	—
Cl	97·9	96·1	93·6	—	—	—	104
$\frac{1}{2}SO_4$	—	—	—	87·7	87·7	87·7	—

B. D. Steele[1] has extended Masson's method by the discovery that, under certain conditions of concentration and potential gradient, the boundary between two colourless solutions, owing to the difference in refractive index, is clearly visible. He has also freed the method from the disturbing influence of jellies by placing the solution to be examined in

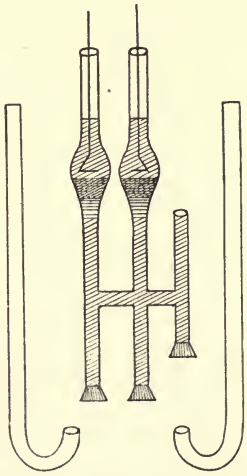


Fig. 56.

[1] *Phil. Trans.* A, CXCVIII. 105 (1902).

the limbs of the glass apparatus of figure 56, and confining it between two partitions of jelly, containing the indicator solutions, aqueous solutions of which are also poured into the tubes above the jelly walls and contain the electrodes. When the current flows, the indicator ions leave the jellies, and enter the liquid columns, after which their velocities cannot be influenced by the presence of the jelly. If the indicator solutions have densities greater than that of the other, the rubber stoppers closing the bottom of the apparatus are removed, and the tubes shown at the sides are inserted. The indicator ions can thus be made to enter the solution from below.

Steele's results for the migration constants agree well with the best of those obtained by the method of Hittorf, and generally with those obtained by the method of Masson. From appreciable differences in certain cases it is, however, concluded that the jelly of Masson's experiments affects the two ions unequally.

The following selection from Steele's results may be given:

Salt	Concentration	Migration constant		
		Steele	Masson	Hittorf, etc.
KCl	0·5	0·490	0·495	—
	1·0	0·488	0·490	0·515
	2·0	0·489	0·483	—
NaCl	0·5	0·597	0·598	0·626
	1·0	0·591	0·595	0·637
	2·0	0·590	0·587	0·642
$BaCl_2$	0·5	0·576	—	0·615
	1·0	0·619	—	0·640
	2·0	0·633	—	0·657
$MgSO_4$	0·184	0·646	—	0·660
	0·5	0·693	0·684	0·700
	1·0	0·715	0·703	0·740
	2·0	0·737	0·693	0·750
	2·0	—	0·688	—

Steele has also calculated from his results the absolute ionic mobilities of some ions and compared the numbers with those

of Kohlrausch, obtaining in most cases a satisfactory agreement. As examples:

Salt	Concentration	u_1		v_1	
		Kohlrausch	Steele	Kohlrausch	Steele
KCl	0·5	0·000512	0·000553	0·000543	0·000529
	2·0	0·000466	0·000483	0·000494	0·000458
NaCl	1·0	0·000285	0·000318	0·000485	0·000452
	2·0	0·000250	0·000274	0·000418	0·000395
$BaCl_2$	0·5	0·000310	0·000330	0·000494	0·000450
	1·0	0·000264	0·000283	0·000405	0·000457
	2·0	0·000213	0·000231	0·000411	0·000398
$MgSO_4$	0·18	0·000155	0·000167	0·000301	0·000304
	0·5	0·000111	117	257	264
	1·0	0·000078	087	221	217
	2·0	0·000054	061	168	178

Influence of Concentration.

The agreement with theory of all experimental measurements of the ionic mobilities of simple monovalent salts, as made by different observers, is a striking confirmation of the truth of the fundamental ideas which underlie Kohlrausch's treatment of the subject. As the concentration of solutions of these salts increases, both the theoretical and the experimental mobilities are seen to diminish, and still to show a satisfactory agreement. Whatever the cause of the decrease of equivalent conductivity with increasing concentration may be, Kohlrausch's theory still gives the true value of the actual velocities with which the ions on the average move through the liquid under the conditions of the experiment, though these velocities are less than those acquired by the action of the same electric forces in dilute solutions.

If we still wish to express the results in terms of the specific ionic mobilities, that is, in terms of the ionic velocities (u_∞ and v_∞) at infinite dilution under unit potential gradient, we must, for these more concentrated solutions, introduce a factor α measuring the ratio of the actual to the limiting

values of the sum of the ionic mobilities. Then, from equation 38, page 214, we have

$$\alpha(u_\infty + v_\infty) = 1{\cdot}037 \times 10^{-2}\frac{k}{n}$$

or

$$\frac{k}{n} = 96{\cdot}44\,\alpha(u_\infty + v_\infty).$$

The coefficient α is thus given by the ratio between the actual value of the equivalent conductivity of the solution and its value at infinite dilution, and can readily be determined experimentally.

Now there seem to be two causes which could reduce the velocities of the ions. If we look on the passage of the ions through the solution as analogous to the motion of bodies through a viscous medium, we see that the frictional forces will increase with the velocity till they become equal and opposite to the driving forces producing the motion. The ions will then travel with constant velocity, and the resistance for such minute bodies being relatively enormous, this limiting velocity will be reached practically instantaneously. An increase in this viscosity, or a decrease in what may be called the ionic fluidity, would therefore diminish the velocity of the ions, and consequently the conductivity of the solution. Chiefly to this cause is to be assigned the variation of ionic velocity, and therefore of conductivity, with temperature. Heating a solution seems to increase the ionic fluidity to about the same extent as it diminishes the ordinary or molar viscosity. Nevertheless Arrhenius has shown that there is no sudden change in the conductivity of a jelly solution at the moment when, by cooling or by the addition of more gelatine, the jelly "sets."[1] While this result certainly proves that no exact connexion exists between the ionic fluidity and the molar viscosity, it does not imply that the ionic fluidity is not affected by the addition of more of the electrolyte, which might affect the molecular condition of the system. This leads to the consideration of another method in which the ionic velocities might be reduced. In developing the theory, the assumption is made that all the substance dissolved is actively concerned in conveying

[1] *B. A. Report*, 1886, p. 344.

the current, though it is possible that such is not always the case. It may be that, under certain conditions of temperature and concentration, a certain fraction of the solute is in a state of inactivity, which must mean that its ions do not drift in opposite directions under the influence of electromotive forces. If, for the present, we exclude the consideration of complex ions, these inactive molecules will be unaffected by the electric forces, and will have no drift in either direction. Now, whatever be the cause of the activity or non-activity of the solute, it is certain that the equilibrium between active and inactive molecules must be a mobile equilibrium, molecules continually passing from one state to the other[1]. Each ion will sometimes be active and sometimes be inactive; while active it will move and while inactive be stationary, and the net result will be that its effective velocity will be reduced in the ratio of the active time to the whole time.

Thus the velocities of simple ions may be reduced by an increase in frictional resistance, by a diminution in the fraction of the dissolved substance which is, at any moment, active, or by a combination of both these causes. In dilute solutions, the resistance offered by the liquid to the passage of the ions through it is probably sensibly the same as in pure water; but when the proportion of non-ionized molecules becomes considerable, we cannot assume that this is the case. If, however, no complex ions are present and the solution is dilute enough for the friction to be taken as constant, the coefficient α can be given a very simple physical meaning. The fraction which expresses the ratio of the actual to the limiting velocity of the ions must then also express the fraction of the dissolved substance which is, at any moment, electrolytically effective, and consequently the fraction of its time during which, on the average, any ion remains active. This fractional number may be called the coefficient of ionization.

Thus, although we can, if we like, always put Kohlrausch's theory in the form shown in our last equation, the constant α will only have a definite physical meaning when no complex ions are present, and the solution is so dilute that the ionic

[1] Whetham, *Phil. Mag.*, July, 1891; *Phil. Trans.*, A, CLXXXIV. 340 (1893).

viscosity keeps constant. This caution is necessary, for it seems to be often assumed that α, as deduced from the ratio of the actual to the limiting equivalent conductivity, always expresses the ionization of the solution, whatever its concentration may be, although for fairly strong solutions no convincing evidence has been adduced in favour of the assumption made.

On the other hand, equation (38) given on p. 214,

$$u_1 + v_1 = 1{\cdot}037 \times 10^{-2} \times \frac{k}{n}$$

in which u_1 and v_1 denote the actual mobilities of the ions under the conditions of the experiment, probably holds good whatever be the concentration of the solution, and gives the simplest and most certain form of Kohlrausch's theory.

Complex ions.

Hittorf himself recognized that the migration constant of cadmium iodide requires the supposition of complex ions, some unaltered salt migrating in company with the iodine, as a complex anion. There is considerable evidence besides that already described that similar ions exist in many other solutions in water and other solvents[1]. This evidence may be summarized as follows:

(1) In the case of simple salts such as potassium chloride, Hittorf's transport number is independent of the concentration, but this is not so for more complicated salts such as barium chloride or magnesium sulphate. The change is so great that it is not easy to explain it by a difference in the variation of the mobility of the two ions with concentration.

(2) While it is possible to assign a definite specific mobility to the ions of potassium chloride and similar salts, the velocities of the ions of more complex salts depend on the nature of the other ion present, until the dilution becomes almost infinite.

(3) In direct measurements of ionic mobilities by the method of moving boundaries, the results agree better with theory for the simple salts, and when the solutions of the more complex salts are of considerable concentration, the phenomena at the boundaries become very complicated.

[1] Whetham, *Phil. Trans.* A, CLXXXIV. 358 (1893); Steele, *Phil. Trans.* A, CXCVIII. 133 (1902); Schlundt, *Jour. Phys. Chem.* VI. 159 (1902).

(4) As we shall see later, the ionization as calculated from the electrical conductivity agrees better with that deduced from the freezing point in the case of simple salts than for more complicated ones.

All these relations are easily explained by the supposition that, as the concentration increases, many solutions, especially of such salts as magnesium sulphate, contain complex ions, formed by the union of some unaltered salt molecules with the anion or cation.

Such molecules of salt will be dragged forwards with the ions and may increase the effective resistance to their motion, thus reducing the velocity below the value given by the fraction indicated above, which expresses the ratio of the active to the total solute at any moment. The ratio of the actual to the limiting velocity then ceases to be equal to the ratio of the average active time to the whole time for each ion. The equilibrium will still be dynamical, however, and these attached molecules must in turn become inactive stationary molecules and active molecules, the parts of which are moving ions. The life of an ion can then be divided into four parts, (1) the time during which it is active as a simple ion, and therefore moving with nearly the velocity it would have in pure water, (2) the time when it is part of an inactive molecule at rest, (3) the time it has an inactive molecule attached to it, and is therefore moving with a velocity smaller than that referred to above, and (4) the time during which it forms part of an inactive molecule dragged along by an active ion, when it moves with the same diminished velocity but is ineffective as far as carrying current is concerned.

The effective or resultant velocity of an ion is found by dividing the average distance it travels during the periods (1) and (3) by the whole time considered, for during the periods (2) and (4) it does nothing towards carrying the current. The effective velocities, as thus calculated, will be correctly determined by Kohlrausch's equation

$$u_1 + v_1 = 0{\cdot}01037 \times \frac{k}{n} \times \frac{dP}{dx}.$$

But when we wish from this result to calculate the

individual values of u_1 and v_1, we must use the migration constant for the given electrolyte, which has been determined by the method of Hittorf. Now the theory of Hittorf's method (page 208) assumes that the difference produced in the concentrations of the liquids round the two electrodes is, in general, entirely due to a difference in the velocities of the two ions; though, as we stated, Hittorf recognized the action of complex ions in exceptional cases. But the differences in concentration might always be explained by the supposition that inactive solute or solvent molecules were attached to one or other of the ions. If this were the case, the division of the value of $u_1 + v_1$ in the ratio of Hittorf's number would lead to an erroneous result for the individual ionic velocities. The calculated velocities would then differ from those experimentally determined by a greater and greater extent, as such complex ions became more numerous owing to an increase in concentration or to other causes. We may thus explain the fact that the experimental results agree less nearly with the calculated ionic velocities in solutions such as those of magnesium sulphate than in solutions of potassium chloride and similar salts.

It will now be evident that, if complex ions are present, the mobility of an ion calculated from observations on solutions of different salts containing it will not be constant, since different numbers of complex ions may exist in the different solutions. Moreover, in the solutions of any one substance, the number of complexes depends on the concentration, as the change in the transport number indicates, and therefore the mobility at infinite dilution cannot be calculated unless the transport number has been determined for a solution dilute enough to secure the absence of complex ions. Experiments on transport numbers have not usually been made in very dilute solutions, and consequently the values for the mobility of such an ion as barium, found by experiments on different solutions of two or more of its salts, do not in general agree with each other. Steele points out, in this connexion, that recent transport experiments by Noyes on solutions of barium chloride and nitrate at a concentration of 0·02 normal give the same mobility to the barium ion in the two solutions. At greater

concentrations, the relative amount of salt taken from the neighbourhood of the cathode (p. 212) is increased. This result might be explained by the assumption that some double molecules of composition $2BaCl_2$ exist, which yield the ions $\overset{+}{Ba}$, $\overset{-}{Cl}$ and $(BaCl_2)\overset{-}{Cl}$. The effects of complex ions will again be considered in Chapter XII.

Connexion between the mobility of an ion and its chemical constitution.

We may conclude, from the experimental confirmation described above, that the velocity of an ion of a simple salt, as calculated by Kohlrausch's theory from the conductivity, really does represent the actual speed with which, on the average, the ion makes its way through the solution. We may therefore apply the theory with confidence to cases in which the experimental confirmation would be difficult or impossible.

If we know the specific velocity of any one ion, we can, from the conductivity of very dilute solutions, at once deduce the velocity of any other ion with which it may be combined, without having to determine the migration constant of the compound, a matter often involving considerable trouble. Thus, taking the specific ionic mobility of hydrogen as 0·0032 cm. per sec. per volt per cm., we can, by determining the conductivity of dilute solutions of any acid, at once find the specific velocity of the acid radicle involved. Or, again, since we know the specific velocity of the silver ion, we can find the velocities of a series of acid radicles at great dilution by measuring the conductivity of their silver salts.

By these methods Ostwald, Bredig, and other observers have found the specific velocities of many ions both of inorganic and organic compounds, and examined the relation between constitution and ionic mobility. A full account of such data has been given by Bredig[1]. The velocities given by him are relative numbers calculated from the conductivities measured in terms of mercury units, and so must be multiplied by 110×10^{-7} if they are wanted in centimetres per second per volt per centimetre.

The mobility of elementary ions is found to be a periodic

[1] *Zeits. phys. Chem.* XIII. 191 (1894).

function of the atomic weight, similar elements lying on similar portions of the wavy curve. The curve much resembles that giving the relation between atomic weight and viscosity in solution. For compound ions the mobility is largely an additive property; to a continuous additive change in the composition of the ion corresponds a continuous but decreasing change in the mobility. Ostwald's results for the formic acid series give

		Diff. for CH_2
Formic acid	HCO'_2 51·2	−12·9
Acetic „	$H_3C_2O_2$ 38·3	− 4·0
Propionic „	$H_5C_3O'_2$ 34·3	− 3·5
Butyric „	$H_7C_4O_2$ 30·8	− 2·0
Valeric „	$H_9C_5O'_2$ 28·8	− 1·4
Caprionic „	$H_{11}C_6O'_2$ 27·4	

Bredig finds similar relations for every such series of compounds which he examined. Isomeric ions of analogous constitution have equal mobilities. A retarding effect is, in general, produced by the replacement of H by Cl, Br, I, CH_3, NH_2 or NO_2: of any element by an analogous one of higher atomic weight (except O and S); of NH_3 by H_2O; of $(CN)_6$ by $(C_2O_4)_3$; by the change of amines into acids; of sulphonic acids into carboxylic acids; acids into cyanamides, dicarboxylic into monocarboxylic acids; and by monamines into diamines. The additive effect is, however, largely influenced by constitution. Thus in metamerides the mobility increases with the symmetry of the ion, especially as the number of C – N unions gets greater.

Conductivity of liquid films.

Reinold and Rücker have investigated the electrical resistance of thin soap films[1]. The thickness was measured by optical means, depending on the interference of two parts of a beam of light. One part of the light passed through a tube across which several films were stretched, and the consequent optical retardation was determined. On the assumption that the refractive index of a film is the same as that of the liquid in bulk, an assumption for which reasons are given, these measurements enable the aggregate thickness of the films to be estimated. It was found that when the films became too thin to reflect light and therefore, like the central spot of a system of Newton's rings, looked

[1] *Phil. Trans.* A. CLXXXIV. 505 (1893).

black by reflected light, no further reduction in thickness could be obtained, and the thickness remained constant for any given liquid. If some salt was added to the liquid, the thickness decreased; thus the following table shows the thickness in micro-millimetres (metres $\times 10^{-10}$) of films of 1 part of hard soap in 40 parts of water with varying amounts of potassium nitrate.

Optical method.

Percentage of KNO_3	3	1	0·5	0
Thickness in $\mu\mu$	12·4	13·5	14·5	22·1

If the conductivity of the film is the same as that of the liquid in bulk, the electrical resistance of a film should give values for the thickness which agree with these numbers. It was found that, as long as the amount of salt present was greater than about 2 or 3 per cent., the results of the two methods agreed, but that, if the amount was less, the electrical method gave a result greater than that obtained optically.

Electrical method.

Percentage of KNO_3	3	2	1	0·5	0
Thickness in $\mu\mu$	10·6	12·7	24·4	26·5	148

These results indicate that the conductivity of a thin film is much greater than that of the liquid in bulk when the concentration of the dissolved electrolyte is very small, but that the conductivities become identical as the concentration increases.

The phenomenon cannot be explained by supposing that the effect of the surface energy is to increase the ionization, because it is in dilute solutions, where the ionization is already nearly complete, that the difference is most marked. Unless the presence of the soap has a disturbing influence, it seems that the ionic friction must be less, and the ionic mobilities greater, in the film than in the bulk of the liquid. It is worthy of note that there is evidence to show that the conductivity of a thin metallic film is less than that of the metal in bulk. On the electron theory this is explained by the interference with the motions of the corpuscles which results when the thickness of the conductor becomes comparable with the mean free path[1].

[1] Longden, *Amer. Journ. Sci.* IX. 407 (1900); *Phys. Rev.* July & Aug. (1900).

CHAPTER X.

GALVANIC CELLS.

Introduction. Reversible cells. Electromotive force. Effect of pressure. Concentration cells. Different concentrations of the electrodes. Different concentrations of the solutions. Concentration double cells. Effect of low concentrations. Chemical cells. Oxidation and reduction cells. Transition cells. Irreversible cells. Secondary cells or accumulators.

Introduction.

SINCE the invention of Volta's pile in the year 1800 many forms of battery have been introduced. An account of those now in use, and of the purposes to which each is specially adapted, may be found in any book on practical electricity. We shall here confine ourselves to the theory of the production of the electric current to be obtained from such cells.

When two metallic conductors are placed in an electrolyte, a current will flow through a wire connecting them provided that a difference of any kind exists between the two conductors in the nature either of the metals or of the portions of the electrolyte which surround them. A current can be obtained by the combination of two metals in the same electrolyte, of two metals in different electrolytes, of the same metal in different electrolytes[1], or of the same metal in solutions of the same electrolyte at different concentrations.

[1] An effective difference in the electrolytes can be secured by dissolving either different substances in the same solvent, or the same substance in different solvents.

In order that the current should be maintained, and the electromotive force of the cell remain constant during action, it is necessary to insure that the changes in the cell, chemical or other, which produce the current, should neither destroy the difference between the electrodes, nor coat either electrode with a non-conducting layer through which the current cannot pass. As an example of a successful cell of fairly constant electromotive force we may take that of Daniell, which consists of the electrical arrangement

zinc / zinc sulphate solution / copper sulphate solution / copper,

the two solutions being usually separated by a pot of porous earthenware. When the zinc and the copper plates are connected through a wire, a current flows, the conventionally positive electricity passing from copper to zinc in the wire and from zinc to copper through the cell. Zinc dissolves, and zinc replaces an equivalent amount of copper in solution, copper being simultaneously deposited on the copper electrode. The internal rearrangements which accompany the production of a current do not cause any change in the original nature of the electrodes, and, as long as a moderate current flows, the only variation in the cell is the appearance of zinc sulphate on the copper side of the porous wall. As long as the supply of copper sulphate is maintained, copper, being more easily separated from its solution than zinc, is alone deposited at the cathode, and the cell remains constant. On the other hand, if no current be allowed to flow, slow processes of diffusion, unchecked by migration in the opposite direction, will cause copper to appear in the anode vessel, and finally to be deposited on the zinc. Little local galvanic cells are thus formed on the surface of the zinc, which then dissolves even though the circuit of the main cell is not completed. Till this deposition occurs, the cell can be left on open circuit without waste, and no zinc will dissolve if it is chemically pure. If however commercial zinc, which contains iron, be used, local action is again set up. This action can be prevented by amalgamating the zinc; probably because that process produces a uniform surface, iron being insoluble in mercury.

The conditions necessary for the continuous production of a current are well illustrated in an experiment described by Ostwald[1]. Plates of platinum and amalgamated zinc are separated by a porous pot, and are each surrounded by some of the same solution of a neutral salt of a metal more oxidizable than zinc, such as potassium sulphate. When the plates are connected together by a wire, no permanent current flows and no appreciable quantity of zinc is dissolved, for any current must primarily liberate potassium at the platinum, the potassium secondarily decomposing water. This primary process would absorb more energy than is supplied by the solution of the zinc. If sulphuric acid be added to the vessel containing the zinc, these conditions are unaltered, and still no zinc is dissolved. On the other hand, if a few drops of acid be added to the vessel in which is the platinum plate, bubbles of hydrogen at once appear, a continuous current flows, and zinc is simultaneously dissolved. This experiment illustrates two conditions necessary for the production of a current. In order that positively electrified ions may enter a solution, an equivalent amount of other positive ions must be removed or negative ions be added; and, for the process to occur spontaneously, the possible actions at the two electrodes must involve a decrease in the total available energy of the system.

Reversible cells.

Considered thermodynamically, galvanic cells must be divided into reversible and non-reversible systems. If the slow processes of diffusion be ignored, the Daniell cell already described may be taken as a type of a reversible cell. Let an electromotive force exactly equal to that of the cell be applied to it in the reverse direction. When the applied force is diminished by an infinitesimal amount, the cell produces a current in the usual direction, and the ordinary chemical changes occur. If the external electromotive force exceeds that of the cell by ever so little, a current flows in the opposite direction, and all the former chemical changes are reversed, copper dissolving from the copper plate,

[1] *Phil. Mag.* [5] xxxii. 145 (1891).

while zinc is deposited on the zinc plate. The cell together with this balancing electromotive force is thus a reversible system in true equilibrium, and the thermodynamical reasoning applied to such systems in the first chapter can be used to examine its properties.

Another reversible cell of similar type is the arrangement

zinc / zinc sulphate / zinc sulphate with mercurous sulphate / mercury

due to Latimer Clark. It is used as a standard of electromotive force, giving 1·434 volts at 15° C. The very slightly soluble mercurous sulphate acts as depolarizer, depositing mercury on the cathode, when the cell works in its natural direction. Here also a reversal of the current reverses all the internal changes of the cell.

Cells from which gas is lost into the atmosphere, such as Volta's original zinc / dilute acid / copper couple, and others in which irreversible processes of reduction occur, such as the Grove arrangement, zinc / dilute suphuric acid / nitric acid / platinum, form essentially irreversible systems. Moreover, it does not follow that, because an accumulator can be used to give a current in the reverse direction to the charging current, it is in the thermodynamic sense a reversible cell. This is only the case when an electromotive force greater by an indefinitely small amount than the secondary electromotive force of the cell will reverse the current through it and the chemical actions in it also. For this to be possible, it is necessary that the whole of the energy of the charging current should be put into available energy of chemical separation, which can all be regained when the cell is discharged.

Electromotive force.

Let us now apply the thermodynamic relations, which we have established in Chapter I., to investigate the electromotive force of reversible cells. The solution of this problem was given in different ways by Willard Gibbs and von Helmholtz. For us the simplest method will be to use the available energy equation which was obtained on p. 29.

Let E denote the electromotive force of the cell at a temperature θ, and let a quantity q of electricity pass reversibly through the cell in the natural direction. The external work done is then equal to Eq, which therefore represents the decrease in the available energy of the system. Thus the equation (11) of available energy

$$\psi = \epsilon + \theta \frac{d\psi}{d\theta},$$

becomes

$$Eq = \epsilon + q\theta \frac{dE}{d\theta}.$$

The decrease ϵ of the internal energy of the cell will be the same if the final state of the system is reached in any other way, as for instance by direct chemical action, the energy equivalent of which can be found by measuring the heat evolved by the reactions. Let λ' be the heat of reaction per gram-equivalent corresponding to the chemical changes which occur, and let q denote the number of electrical units simultaneously passed through the cell; then we get

$$Eq = \lambda' + q\theta \frac{dE}{d\theta},$$

or

$$E = \frac{\lambda'}{q} + \theta \frac{dE}{d\theta}.$$

Writing λ for $\frac{\lambda'}{q}$ we have

$$E = \lambda + \theta \frac{dE}{d\theta} \quad \text{.....(39)}$$

as the expression for the electromotive force of the cell, where λ denotes the calorimetric heat of reaction which would correspond to unit electric transfer.

The same equation can of course be obtained in other ways, as for instance by putting the cell through a complete ideal reversible cycle of changes in the manner of Carnot's engine, the external work here being done by the energy of the current.

It will be observed that if the temperature coefficient $dE/d\theta$ is zero, the equation shows that the electromotive force

is equal to the heat of reaction. The earliest formulation of the subject, due to Lord Kelvin, assumed that this relation was true in all cases; as, calculated in this way, the electromotive force of the Daniell cell, which has a very small temperature coefficient, agreed with observation. The heat of reaction when one electrochemical equivalent of zinc replaces copper in sulphate solution, which is the effective process of the cell, is 2·592 calories. Multiplying by the mechanical equivalent of the calorie, $4{\cdot}18 \times 10^7$, we have $1{\cdot}09 \times 10^8$ electromagnetic units, or 1·09 volts, a number agreeing with that observed.

In cases in which the temperature coefficient is appreciable, the exact expression must be used. It has been experimentally confirmed by Czapski[1] and Gockel[2], and quantitatively by Jahn[3]; it has been verified for the Grove gas cell by Smale[4], and for cells in which fused salts instead of solutions are used as electrolytes by L. Poincaré[5], J. Brown[6], and Buscemi[7]. It is clear, since the electrical energy is not equal to the heat of reaction in the equation, that there must be a reversible evolution or absorption of heat energy in the cell per unit electric transfer equal to the thermal equivalent of the expression $\theta \frac{dE}{d\theta}$. This reversible heat is to be distinguished from the irreversible heat produced in a cell by the passage of a current through it against the resistance. The latter depends on the square of the current, and can therefore be reduced to any extent, as compared with the reversible heat, by lowering the strength of the current. Jahn compared the reversible heat thus calculated from the electromotive force and its temperature coefficient, with that found by means of experiments with an ice calorimeter.

[1] *Wied. Ann.* XXI. 209 (1884).
[2] *Wied. Ann.* XXIV. 618 (1885).
[3] *Wied. Ann.* XXVIII. 21 (1886).
[4] *Zeits. phys. Chem.* XIV. 577 (1894).
[5] *Paris Reports*, II. 411; *Compt. rend.* CX. 339 (1890); *Ann. Chim. et Phys.* [6] XXI. 344 (1890).
[6] *Proc. R. S.* LII. 75 (1892).
[7] *Att. Accad. in Catania*, XII. (1900).

The following table gives some of his results:

Cells	E.M.F. at 0°. Volts	$dE/d\theta$	Electric energy in calories	Heat of reaction in calories	Reversible heat effect	
					Calculated	Observed
$Cu/CuSO_4.100H_2O/ZnSO_4.100H_2O/Zn$	1·096	+0·000034	50526	50110	− 428	− 416
$Ag/AgCl/ZnCl_2.100H_2O/Zn$	1·031	−0·000409	47506	52170	+5148	+4660
$Ag/AgNO_3.100H_2O/Pb(NO_3)_2.100H_2O/Pb$	0·932	.....	42980	50870	+7890	+7950
$Ag/AgNO_3.100H_2O/Cu(NO_3)_2.100H_2O/Cu$	0·458	.....	21120	30040	+8920	+8920

Certain mercury cells gave results not so concordant with theory, but this want of agreement was afterwards shown by Nernst to be due to an erroneous value for the heats of formation of mercury compounds.

Attempts have been made by Jahn[1] and Gill[2] to localize this reversible heat by measuring the Peltier effect at the junctions in the cell. They find that the usual thermo-electric equation, which we shall consider in the next chapter, giving the sum of the Peltier effects

$$\Sigma(\pi) = -\theta \frac{dE}{d\theta},$$

holds good within the limits of experimental error.

The relation

$$E = \lambda + \theta \frac{dE}{d\theta}$$

then becomes

$$E = \lambda - \Sigma(\pi) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (40),$$

so that

$$\lambda = E + \Sigma(\pi) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (41).$$

The relation thus verified has been applied by Jahn to the determination of heats of formation[3].

[1] *Wied. Ann.* XXXIV. 755 (1888) and L. 189 (1893).
[2] *Wied. Ann.* XL. 115 (1890).
[3] *Wied. Ann.* XXXVII. 408 (1889).

Effect of Pressure.

Whenever the action of a cell causes change of volume, the electromotive force must depend on the external pressure[1]. In cells where metals only are deposited or dissolved, the changes in volume are small; but when gases are evolved or condensed at either electrode, a considerable amount of external work is done. In treating this problem from the point of view of thermodynamics, we naturally employ the thermodynamic potential at constant pressure instead of that at constant volume (pp. 23 and 24).

The two thermodynamic principles give, as we have seen, the relation

$$\begin{aligned}\delta\epsilon &= \theta\,\delta\phi + \Sigma\,(X\,\delta x)\\ &= \theta\,\delta\phi + E\,\delta q + p\,\delta v,\end{aligned}$$

since, in this case, the external work comprises a term $p\delta v$ as well as the electrical term $E\delta q$. Subtracting $\delta(\theta\phi + pv)$ from each side,

$$\delta(\epsilon - \theta\phi - pv) = E\,\delta q - v\,\delta p - \phi\,\delta\theta,$$

or, writing ζ for $\epsilon - \theta\phi - pv$,

$$\delta\zeta = E\,\delta q - v\,\delta p - \phi\,\delta\theta.$$

The right-hand side is a perfect differential, and we may write

$$\frac{\partial\zeta}{\partial q} = E, \qquad \frac{\partial\zeta}{\partial p} = -v, \qquad \frac{\partial\zeta}{\partial\theta} = -\phi;$$

hence we have relations such as

$$\left(\frac{\partial E}{\partial p}\right)_q = \frac{\partial}{\partial p}\left(\frac{\partial\zeta}{\partial q}\right) = \frac{\partial}{\partial q}\left(\frac{\partial\zeta}{\partial p}\right) = -\left(\frac{\partial v}{\partial q}\right)_p,$$

which prove that the rate of increase of the electromotive force with the pressure is equal to the decrease in volume at constant pressure per unit quantity of electricity passing, when the temperature in each case remains constant. Faraday's law shows that the volume change is proportional to the quantity of electricity, so that if v_1 and v_2 be the initial and final volumes,

$$-\frac{\partial v}{\partial q} = \frac{v_1 - v_2}{q},$$

and we get

$$q\,\frac{\partial E}{\partial p} = v_1 - v_2.$$

[1] See Duhem, *Le potentiel Thermodynamique*, p. 117; and Love, *Report of the Australasian Association*, Sydney, 1898, p. 84.

For solids and liquids v_1 and v_2 are sensibly independent of the pressure, and we get by integration for the change of electromotive force with change of pressure

$$E_2 - E_1 = \frac{v_1 - v_2}{q}(p_2 - p_1) \quad \ldots\ldots\ldots\ldots (42).$$

In the case of gases, if Boyle's law be assumed, we can again readily integrate the equation. Let us as usual denote by R the gas constant for one gram-molecule, so that the value of R is the same for all gases. Let each molecule of gas dissolve as n ions; let the valency of each ion be y, and let q be the amount of electric charge on one gram-atom of a monovalent ion. The electric transfer required to liberate one gram-molecule of the gas is then qny. We thus obtain

$$E_2 - E_1 = \int_{p_1}^{p_2} \frac{v}{qny}\,dp = \frac{RT}{qny}\int_{p_1}^{p_2} \frac{dp}{p} = \frac{RT}{qny}\log\frac{p_2}{p_1} \ldots (43).$$

The decomposition of water with platinized electrodes is a reversible process, so that this equation also determines the effect of pressure on the decomposition point of water.

These two relations (42) and (43) have been experimentally confirmed by Gilbault[1] throughout a range of pressure extending from 1 to 500 atmospheres. The effect for a Daniell cell is about the hundredth part of that for a gas battery.

Many of the results here deduced thermodynamically can be obtained in other ways. Thus J. J. Thomson[2] has found the effect of pressure on the electromotive force of gas cells by an application of the Lagrangian function in a strictly dynamical way, and, by making a probable assumption, has also obtained Helmholtz's equation in a similar manner. Again, as we shall see later, Nernst and Planck have developed a theory of galvanic cells from a knowledge of the velocities of the ions and the osmotic pressures.

[1] *Ann. Fac. des Sci. de Toulouse*, v. A.S. 1891.

[2] *Applications of Dynamics to Physics and Chemistry*, pp. 86, 98.

Concentration cells.

As stated above, an electromotive force is produced whenever there is a difference of any kind at two electrodes immersed in electrolytes. In ordinary cells the difference is secured by using two dissimilar metals, but an electromotive force also exists if two plates of the same metal are placed in solutions of different substances, or of the same substance at different concentrations. Another method is to use in the same solution electrodes of different concentration. Such electrodes can be constructed by taking hydrogen in contact with platinized platinum, and making the pressure different at the two ends.

In all such cells the electrical energy is not obtained from chemical changes, but from the energy of expansion of substances from greater to smaller concentrations. For the cases in which very dilute substances, gaseous or dissolved, alone are used, the gaseous laws are obeyed, and there is consequently no heat of dilution. Thus in Helmholtz's general equation, which is applicable to all kinds of cell, namely

$$E = \lambda + \theta \frac{dE}{d\theta},$$

λ vanishes, and we get

$$E = \theta \frac{dE}{d\theta} \text{ or } \frac{dE}{E} = \frac{d\theta}{\theta};$$

so that integrating,

$$\log E = \log \theta + \text{constant},$$

or

$$E = C\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (44).$$

The electromotive force is therefore proportional to the absolute temperature. This relation, it will be noticed, depends on the absence of chemical action or heat of dilution, and is only true, even for concentration cells, when the substances are so dilute that no sensible heat is evolved on further dilution. Concentration cells, in which it holds, are really heat engines, and work by using the heat energy of their surroundings. These remarks apply to all concentration cells for which the gaseous laws hold, whether the difference in concentrations is in the electrodes or in the solutions.

The nature and theory of concentration cells were first fully discussed by von Helmholtz by an application of the principles of thermodynamics and a knowledge of the phenomena of vapour pressure[1], without any special electrolytic hypotheses, and the general accuracy of his theory was confirmed by the experiments of Moser[2].

Different concentrations of the electrodes.

Let us consider the example mentioned, hydrogen electrodes at different pressures. If these electrodes are immersed in a solution of acid or alkali, a current will flow, gas dissolving at the electrode of high pressure and appearing at that of low pressure. Now a thermodynamic cycle can be performed at constant temperature by allowing such a current to flow reversibly against a balancing electromotive force, taking out the gas evolved, slowly compressing it, and then passing it into the other electrode vessel till everything is in its initial condition.

The work gained from the gas during its escape at constant pressure from the first electrode vessel is $p_1 v_1$. In compressing it from p_1 to p_2 the work gained is $-\int_{p_1}^{p_2} p\,dv$, as was shown on p. 3. Finally in passing it into the second electrode vessel the gas does work $-p_2 v_2$. The total work may be written

$$\left[pv\right]_2^1 - \int_{p_1}^{p_2} p\,dv.$$

Now

$$\delta(pv) = p\delta v + v\delta p,$$

so that

$$\int v\,dp = \left[pv\right]_2^1 - \int p\,dv.$$

Thus the work done during the process under consideration is always measured by $\int_{p_1}^{p_2} v\,dp$; and only if Boyle's law holds, so that $\left[pv\right]_2^1$ vanishes, can it also be expressed as $-\int_{p_1}^{p_2} p\,dv$.

[1] *Wied. Ann.* III. 201 (1878); *Ges. Abhand.* I. 840, II. 979; *Sitzungsber. Berl. Akad.* Juli 1882.

[2] *Wied. Ann.* III. 201 (1878).

Then, as before, let each molecule of the gas dissolve as n ions, the average valency of which is y; q being the electric charge on one gram-atom of a monovalent ion, the electric transfer required to liberate one gram-molecule of the gas is qny. In the complete cycle of the concentration cell, both the electrical process and the reverse operations can be performed isothermally, so that the balance of work gained must be zero, and we may write

$$Eqny + \int_{p_1}^{p_2} v\,dp = 0.$$

This result is general; but if the gas obeys Boyle's and Charles' laws we may put

$$pv = RT,$$

and obtain

$$E = -\frac{RT}{qny}\int_{p_1}^{p_2}\frac{dp}{p} = -\frac{RT}{qny}\log_e\frac{p_2}{p_1} \quad \ldots\ldots\ldots\ldots (45),$$

an equation which shows that the electromotive force of the cell described is proportional to the logarithm of the ratio of the pressures at the two electrodes. It seems that no quantitative experiments have yet been made on such cells, and this relation therefore remains without practical confirmation. The method of deducing it, however, will serve later on to elucidate other more complicated cases.

A cell similar in theory, in which the hydrogen is replaced by mercury, has been experimentally realized. The electrodes consist of a long and a short column of mercury, each separated from the solution of a mercurous salt by parchment paper, which is impervious to the mercury in bulk but apparently allows it to pass in the form of ions. Mercury dissolves from the column of high pressure, and is precipitated beneath the column of low pressure, a corresponding electric current passing through the cell. The process can be mechanically reversed by raising the required quantity of mercury through a height h equal to the difference in level of the two columns, and the electrical work gained is equal to the work so expended. Thus, if A is the atomic weight in grams,

$$Eqny = Agh,$$

n being in this case equal to unity.

Des Coudres[1] arranged such a cell, and obtained the following results:

Pressure in centimetres	E (calculated)	E (observed)
36	$7{\cdot}2 \times 10^{-6}$ volts	$7{\cdot}4 \times 10^{-6}$ volts
46	9·3 „ „	10·5 „ „
113	23 „ „	21 „ „

Another method of varying the concentration of the electrodes is to use amalgams of a metal, of different proportions. Here again, the passage of material is from a concentrated to a dilute condition; and, if we suppose that metals dissolved in each other exert osmotic pressure like that of ordinary solutions (a hypothesis which is supported by the experiments of Ramsay on the vapour pressures of amalgams and those of Heycock and Neville on the fusion points of various alloys), we can calculate the osmotic work needed to undo the changes produced by the current in exactly the same way in which we calculated the mechanical work in former cases. Assuming that the osmotic pressure is proportional to the concentration c, we get

$$E = \frac{RT}{qny} \log_e \frac{c_2}{c_1}.$$

The electromotive forces of such cells have been determined by G. Meyer[2], who finds a good agreement with theory for amalgams of zinc, cadmium and copper. Thus for zinc amalgam in zinc sulphate solution:

Temp. Cent.	c_2	c_1	E (observed)	E (calculated)
11°·6	0·003366	0·00011305	0·0419 volts	0·0416 volts
67°·5	„	„	0·0516 „	0·0497 „
0°·0	0·002280	0·0000608	0·0452 „	0·0426 „
60°·0	„	„	0·0520 „	0·0519 „

[1] *Wied. Ann.* XLVI. 292 (1892).

[2] *Zeits. phys. Chem.* VII. 447 (1891).

In calculating these numbers, the value for R was taken corresponding to one gram-molecule. Now for metals dissolved in mercury, the vapour pressures show that their molecules consist of one atom each, and therefore the gram-molecule of zinc was taken as Zn or 63·5 grams. The concordance with the observed values therefore confirms the monatomic nature of the molecule of a metal dissolved in mercury.

In both kinds of cell, it is seen from the equation that the electromotive force is independent of the nature of the electrolyte. Again, the equation shows that the electromotive force should be proportional to the absolute temperature, and this result also is confirmed by the experiments. The conditions necessary to secure this result have been already considered on p. 241.

Different concentrations of the solutions.

Of more practical importance is the case of a concentration cell when two plates of the same metal are immersed in solutions of the same salt at different concentrations. Take for example the cell

silver / dilute silver nitrate / concentrated silver nitrate / silver.

Here metal dissolves in the more dilute solution and is deposited from the more concentrated solution. When one electrochemical unit of electricity passes, one gram-equivalent of silver dissolves at the anode and an equal quantity is deposited at the cathode. In this manner the anode vessel must gain one gram-equivalent of salt and the cathode vessel lose the same amount. Now consider the motion of the ions through the solution. The current, which is exclusively carried by silver ions at the electrodes, is shared between silver ions and NO_3 ions in the body of the liquid. If the ionic velocities were the same, therefore, half a gram-equivalent of each would pass across the surface of contact of the solutions. In the general case, when the transport ratio of the anion is r, and that of the cation $1-r$, the anode vessel will, on the whole, gain $1-(1-r)$ or r gram-equivalents of silver and therefore of salt, while the cathode vessel must lose an equal amount, the difference between this case and that considered on p. 208 consisting in the fact that we now have a dissolvable anode.

In order to return these r equivalents of salt from the dilute to the concentrated solution in a reversible manner, osmotic operations can be performed analogous to those required to effect a similar change in the hydrogen electrodes described on p. 242. Let us place the more dilute solution, which has received additional salt by reason of the electric transfer, in an osmotic cylinder, of which the piston is impervious to the salt in question, and is backed by a large volume of the pure solvent. Let the pressure on the piston be that of equilibrium. Allow this pressure to fall by an infinitesimal amount, so that solvent enters the solution till the concentration is again exactly as it was before the electric transfer. The change in concentration is very small if a large volume of solution is present, so that the process practically occurs at constant pressure and the work gained is $P_1 v_1$, where v_1 denotes the change in volume, and P_1 the constant osmotic pressure. Now separate bodily from the solution that volume of it which contains the amount of salt transferred by the current, and reversibly compress this quantity in an osmotic cylinder till its osmotic pressure rises to P_2, that of the more concentrated solution of the cell. The work done by the osmotic forces is $-\int_{P_1}^{P_2} P dv$. Finally place this liquid in contact with the stronger cell solution, connect it through a semi-permeable wall with the reservoir of the pure solvent, and squeeze out solvent till the solution regains its initial volume by the expenditure of work equal to $P_2 v_2$. The thermodynamic cycle is then complete.

Both the electrical and the osmotic processes of this cycle can be made reversible and isothermal; then the balance of external work must vanish. Denoting the electromotive force by E, and considering the electric transfer q, we may write

$$Eq + \Big[Pv\Big]_2^1 - \int_{P_1}^{P_2} P dv = 0,$$

which gives, as on p. 242,

$$Eq = -\int_{P_1}^{P_2} v dP.$$

Now, as before, let q be taken to represent the electric transfer needed to liberate one gram-atom of two opposite monovalent ions at the electrodes, and therefore to decompose one gram-molecule of a monovalent salt. If the salt does not yield two opposite monovalent ions, let y be the total valency of the anions or of the cations obtained from one molecule; for instance, y will be 2, whether the cations be two monovalent ions such as the two $\overset{+}{\mathrm{H}}$ ions of a molecule of sulphuric acid, or one divalent ion such as the $\overset{+}{\mathrm{Cu}}$ of copper sulphate. The total electric transfer corresponding to the decomposition of one gram-molecule of salt and the liberation of one gram-atom of each of the ions is then qy, and we have

$$Eqy = -\int_{P_1}^{P_2} v\,dP \qquad \text{.....(46).}$$

It has been shown above that while one gram-atom of an ion is liberated at the electrode, the transfer of salt from the concentrated to the dilute solution is r, where r is the transport ratio for the anion. Again, as explained on p. 159, the osmotic pressures of electrolytes are abnormally high, so that, when the solutions are dilute, the usual gaseous equation gives

$$Pv = riRT$$

for the amount of salt under consideration, where i is van 't Hoff's osmotic factor. Substituting for v in equation (46) we have

$$Eqy = -RT\int_{P_1}^{P_2} ri\,\frac{dP}{P},$$

or

$$E = -\frac{RT}{qy}\int_{P_1}^{P_2} ri\,\frac{dP}{P} \qquad \text{.....(47).}$$

In general, the factor i is a complicated function of the concentration and therefore of P, so that this integral cannot be directly calculated. A similar expression has been considered in detail by Lehfeldt[1], and made the basis of a method of determining the osmotic pressures of concentrated solutions. If the two concentrations are not very different from each

[1] *Phil. Mag.* [6] 1. 377 (1901).

other, and the solutions moderately dilute, in certain cases no serious error will be involved in the assumption that ri is constant. The last equation then becomes by integration

$$E = -\frac{riRT}{qy}\log_e\frac{P_2}{P_1} \quad \text{.....(48).}$$

Again, for these dilute solutions, the osmotic pressures are proportional to the concentrations c_2 and c_1, and we get

$$E = -\frac{riRT}{qy}\log_e\frac{c_2}{c_1} \quad \text{.....(49).}$$

Finally for very dilute solutions, i, the ratio of the actual to the non-electrolytic value of the osmotic pressure, becomes equal to n the total number of ions given by one molecule of salt. We thus reach the result

$$E = -\frac{rnRT}{qy}\log_e\frac{c_2}{c_1} \quad \text{.....(50),}$$

which is strictly applicable to very dilute solutions only.

This expression can be calculated numerically. For deci- and centi-normal solutions of silver nitrate the transport number r is the same, and has the value 0·528 (p. 212). In a cell containing these liquids,

$$E = \frac{0{\cdot}528 \times 2 \times 8{\cdot}28 \times 10^7 \times 291}{96440 \times 1} \times 2{\cdot}303 \times \log_{10} 10$$

$$= 0{\cdot}060 \times 10^8 \text{ C.G.S. units}$$

$$= 0{\cdot}060 \text{ volts.}$$

Nernst measured the electromotive force of this cell experimentally and found the value 0·055 volt[1]. Considering the restrictions made in developing the equation, this number is in remarkable agreement with the theoretical result.

It will be noticed that the electromotive force of the concentration cells just described, of which the arrangement silver / dilute silver nitrate / concentrated silver nitrate / silver is an example, depends on the migration ratio for the anion.

[1] *Zeits. phys. Chem.* VII. 477 (1891).

A second type of cell can be constructed, the formula for which involves the migration number for the cation. In the system

silver / silver chloride / concentrated potassium chloride / dilute potassium chloride / silver chloride / silver,

the silver chloride is very insoluble, so that the mass of it dissolved, which alone is electrolytically active, is constant, and the two silver junctions are kept always in the same condition. When an electrochemical unit of electricity passes through the cell in the direction from left to right as above, a gram-equivalent of silver dissolves at the first electrode. This metal displaces some of the silver in the chloride, and the silver so liberated forms fresh silver chloride with an equivalent of the chlorine ions of the potassium chloride. A gram-equivalent of this salt is thus removed from the more concentrated solution. At the other end of the chain, silver is deposited from the silver chloride, and a gram-equivalent of potassium chloride must therefore appear in the more dilute solution. But meanwhile chlorine ions have been migrating against the current from the dilute to the concentrated solution; and if r is, as before, the migration ratio for the anion, this process involves a loss of r gram-equivalents of salt at the cathode (see p. 245). The dilute solution, therefore, on the whole, only gains $1 - r$ gram-equivalent, and the concentrated solution must lose an equal amount. Now $1 - r$ is the migration ratio of the cation. It will now be evident that, when we imagine the cycle of operations completed by the osmotic process described on p. 246, we shall arrive at the result

$$E = -\frac{RT}{qy}\int_{P_1}^{P_2}(1-r)\,i\,\frac{dP}{P} \qquad \text{.....(51).}$$

On the approximate assumptions there made we shall get

$$E = -(1-r)\frac{iRT}{qy}\log_e\frac{P_2}{P_1} \qquad \text{.....(52),}$$

or, for very dilute solutions,

$$E = -(1-r)\frac{nRT}{qy}\log_e\frac{c_2}{c_1} \qquad \text{.....(53),}$$

with the same notation previously used.

From an equation equivalent to (52) the following table was constructed by Nernst[1], giving a comparison between the observed and calculated values of the electromotive force of concentration cells. c_1 and c_2 denote the concentrations of the two solutions in gram-equivalents per litre.

Electrolyte	c_1	c_2	E in volts (observed)	E in volts (calculated)
HCl	0·105	0·0180	0·0710	0·0717
,,	0·1	0·01	0·0926	0·0939
HBr	0·126	0·0132	0·0932	0·0917
KCl	0·125	0·0125	0·0532	0·0542
NaCl	0·125	0·0125	0·0402	0·0408
LiCl	0·1	0·01	0·0354	0·0336
NH_4Cl	0·1	0·01	0·0546	0·0531
NaBr	0·125	0·0125	0·0417	0·0404
$NaO_2C_2H_3$	0·125	0·0125	0·066	0·0604
NaOH	0·235	0·030	0·0178	0·0183
NH_4OH	0·305	0·032	0·024	0·0188
KOH	0·1	0·01	0·0348	0·0298

Some of these results have been recalculated by Lodge, with later values for the migration numbers[2]. In some cases the agreement is improved, in others it is made worse. The general result of the comparison is unaltered.

Concentration double cells.

In the cells hitherto described, the process is complicated by the effects of migration, but these effects can be eliminated in a manner due to von Helmholtz. If a calomel cell,

zinc / dilute zinc chloride / mercurous chloride / mercury,

be coupled in the reverse direction with a similar cell in which the zinc chloride is concentrated, the arrangement is equivalent to the chain

Zn / dilute $ZnCl_2$ / HgCl / Hg / HgCl / concentrated $ZnCl_2$ / Zn.

In this double cell there is no migration from one solution of zinc chloride to the other, but a diminution of the amount of

[1] *Zeits. phys. Chem.* IV. 128 (1889).

[2] *Lond. Phys. Soc. Proc.* XVII. 369 (1900); *Phil. Mag.* [5] XLIX. 351 and 454 (1900).

mercurous chloride in the first cell, and an increase of it in the second. Mercurous chloride is very insoluble, and hence its active or dissolved mass remains constant, and the mercury surfaces in the two cells keep always in the same state. The double cell is therefore equivalent to a simple concentration cell

$$\mathrm{Zn}\,/\,\text{dilute}\ \mathrm{ZnCl_2}\,/\,\text{concentrated}\ \mathrm{ZnCl_2}\,/\,\mathrm{Zn},$$

in which the effects of migration are eliminated. Von Helmholtz originally solved the problem of the concentration cell independently of ionization hypotheses by imagining the thermodynamic cycle to be completed by evaporation from the one solution and condensation on to the other.

In this way thermodynamic data only are needed, but it is now simpler to treat the subject by an application of the principles of osmotic pressure and electric ionization as above. An investigation similar to that already used holds good, but, in this case, when one gram-atom of zinc dissolves, one gram-molecule of salt is formed in the dilute solution and decomposed in the more concentrated solution, and this result is not complicated by migration. The transfer of salt, corresponding to unit electrochemical transfer, is therefore unity instead of r, and equation (52) becomes

$$E = \frac{iRT}{qy} \log_e \frac{P_2}{P_1} \qquad \text{.....(54).}$$

If we use very dilute solutions of an electrolyte yielding n ions, the electromotive force of the concentration cell is

$$E = \frac{n \times 8{\cdot}28 \times 10^7 \times 291}{96440 \times y \times 10^8} \times 2{\cdot}303 \times \log_{10} \frac{c_2}{c_1}$$

$$= \frac{n}{y} \times 0{\cdot}0575 \times \log_{10} \frac{c_2}{c_1} \qquad \text{.....(55).}$$

In the double calomel cell described above, the number of ions is three and the valency of the zinc is two, so that when the ratio of concentrations is 10 the electromotive force is 0·0863 volt.

For very dilute solutions of any salt giving two monovalent ions, whatever the absolute concentrations, if the ratio of the concentrations is 10, the electromotive force is theoretically 0·115 volt.

When the concentrations though still small are too great for the ionization to be taken as complete, an approximate result may be obtained from equation (54),

$$E = \frac{iRT}{qy} \log_e \frac{P_2}{P_1},$$

when the actual values of the osmotic pressures P_1 and P_2 and of van 't Hoff's osmotic factor i are known.

Experimental investigations on these double cells have been made by Goodwin[1]; the following are examples of his results.

Zinc chloride / calomel and zinc chloride / silver chloride cells at 25°.

Concentration of the $ZnCl_2$ solutions in fractions of normal		Observed E.M.F. of calomel cells in volts	Observed E.M.F. of silver chloride cells in volts	Calculated E.M.F. in volts
0·2	0·02	0·0787	0·0767	0·0797
0·1	0·01	0·0800	0·0780	0·0818
0·02	0·002	0·0843	0·0843	0·0844
0·01	0·001	0·0861	0·0847	0·0853

Zinc sulphate / lead sulphate cells.

Concentration of the $ZnSO_4$ solutions in fractions of normal		Observed E.M.F. in volts	Calculated E.M.F. in volts
0·2	0·02	0·0427	0·0453
0·1	0·01	0·0440	0·0471
0·02	0·002	0·0522	0·0500

By the use of the concentration double cells described in this section, the effects of migration are eliminated. Another class of concentration cells, invented by Nernst, eliminates all effects except those of migration, and thus enables measurements to be made of the potential difference which exists at the junction of two solutions, differing either in the nature or the concentration of their contents. These cells will be considered in a future chapter under the head of the diffusion of electrolytes.

[1] *Zeits. phys. Chem.* XIII. 577 (1894).

Effect of low concentrations.

The logarithmic formulae for all these concentration cells indicate that theoretically their electromotive force can be increased to any extent by diminishing without limit the concentration of the more dilute solution; $\log P_2/P_1$ then becomes very great. This condition can to some extent be realized in a manner that throws light on the general theory of the subject.

Let us consider the arrangement

Ag / AgCl with normal KCl / KNO_3 / deci-normal $AgNO_3$ / Ag.

The concentration of silver chloride is very small in saturated aqueous solution; from the electric conductivity it has been estimated as 0·0000117 normal. It is still further reduced by the presence of the large excess of chlorine ions of the potassium chloride. According to principles to be explained in a later chapter, the product of the concentrations of the ions divided by the concentration of the non-ionized molecules should be a constant at each temperature, so that the lowering of solubility produced by a solution of potassium chloride of given strength can be calculated. The normal solution used in the example has a coefficient of ionization 0·756; and so the final concentration of the silver ions, in presence of deci-normal potassium chloride, which determines the amount of silver chloride dissolved, is $0{\cdot}0000117^2/0{\cdot}0756$ normal. Putting in this value, allowing for the ionization 0·82 of the silver nitrate solution, and assuming that the presence of the potassium chloride does not affect the osmotic work done by the cell, the electromotive force is calculated as 0·52 volt. This number was experimentally confirmed by Ostwald[1] who also examined other cells with similar electrodes giving high electromotive forces. Thus

1.	Deci-normal silver nitrate /	silver chloride in potassium chloride	0·51 volt
2.	„ „ „ /	ammonia	0·54 „
3.	„ „ „ /	silver bromide in potassium bromide	0·64 „
4.	„ „ „ /	sodium thiosulphate	0·84 „
5.	„ „ „ /	silver iodide in potassium iodide	0·91 „
6.	„ „ „ /	potassium cyanide	1·31 „
7.	„ „ „ /	sodium sulphide	1·36 „

[1] *Lehrbuch*, II. 882.

The effective concentration of the silver can also be reduced by adding some substance which, by combining with the silver ions, removes them as such from solution. This is shown by the high electromotive forces of the cells Nos. 2, 4, and 6 in the above list.

Other metals have been used as electrodes by Zengelis[1], who showed that, in many cases, cells with electrodes of copper, lead, nickel, or cobalt, possessed electromotive forces which were greater the more the concentration of the ions round one electrode was depressed by the addition of a salt.

Hittorf[2] has even shown that the effect of a cyanide round a copper electrode is so great that copper becomes an anode with regard to zinc. Thus the cell

$$Cu / KCN / K_2SO_4 / ZnSO_4 / Zn$$

furnishes a current which carries copper into solution and deposits zinc. In a similar way, silver could be made to act as anode in presence of cadmium.

If we know the concentration of the ions round one electrode, it is possible to calculate it round the other from observations on the electromotive force, and this has been done by Behrend[3].

The success of the theory of such cells as we are now considering confirms the natural hypothesis made in the investigation, namely, that the osmotic pressure to be used in calculating the osmotic work is simply that of the migrating substance, one of the ions of which is the metal of the electrode. In the cell containing silver chloride in potassium chloride, for example, the osmotic pressure which appears in the logarithmic formula is that due to the silver chloride alone, not the total osmotic pressure of the solution round the electrode due to potassium chloride as well. Moreover, if, when the silver ions are dissolved, nearly all of them are at once converted into compound ions, such as the $KAgCy_2$ ions of potassium silver cyanide, the effective concentration and the effective osmotic

[1] *Zeits. phys. Chem.* XII. 298 (1893).

[2] *Zeits. phys. Chem.* X. 592 (1892); see also next chapter.

[3] *Zeits. phys. Chem.* XI. 466 (1893).

pressure are those due to the slight trace of Ag ions left[1], and not the values due to the total concentration of the silver in the solution, whether present as simple or compound ions. It seems that in deducing the formulae by the processes described on pp. 246, 249, we should imagine the osmotic work done against a piston permeable to everything except the actual salt, one of the ions of which is the dissolving electrode. This is probably legitimate, for although such a semi-permeable membrane cannot in every case be practially constructed, its existence would violate no known natural principle, and the thermodynamic reasoning based on its imaginary use would therefore still be valid.

Chemical cells.

The ideas used in developing the theory of concentration cells have been applied to the usual type of galvanic cell by Nernst and others, though in this case the basis of the investigation is more speculative. When a metal is placed in contact with the solution of one of its salts, and a current is passed across the junction and metal dissolved, changes occur in the chemical, osmotic, and electrical energies of the system. As the osmotic pressure of the solution rises, the tendency of the metal to dissolve as electrolytic ions becomes less, and it is suggested that eventually at a certain pressure no further tendency to dissolve would exist. Above this pressure the metal would tend to come out of solution and be deposited. This critical pressure bears no relation to the limit set to the osmotic pressure of a solution by reason of the finite solubility of the salt. With some metals it may be much too high to be ever reached, with others it may be too low. If the concentration of the solution giving the critical pressure

[1] According to Morgan (*Zeits. phys. Chem.* XVII. 513 (1895)), potassium argento-cyanide undergoes ionization in three steps. The first, $KAgCy_2 = \overset{+}{K} + \overset{-}{AgCy_2}$, is nearly complete. A small number of the complex ions $\overset{-}{AgCy_2}$ give $AgCy + \overset{-}{Cy}$, while to an almost infinitesimal extent occurs the third process $AgCy = \overset{+}{Ag} + \overset{-}{Cy}$. The mass of silver in the ionic state in a litre of a one-twentieth normal solution of potassium silver cyanide is estimated as four millionths of a milligram, whereas in a solution of silver nitrate of equivalent concentration, the quantity is 10^9 times as great.

could be obtained, so that there would be no tendency for ions of the metal to enter or leave the liquid, it is fair to conclude that the metal and solution would be electrically neutral to each other, and that no difference of potential would exist between them. This critical osmotic pressure has been called the electrolytic solution pressure of the metal in the given solution. Nernst identifies it with the osmotic pressure of the ions of the metal in the substance of the metal itself. Such an idea is perhaps suggested by the osmotic pressure of certain metals when dissolved in mercury to form amalgams; the use of these amalgams to give electrodes of different concentrations has already been described. On this view the osmotic work done in transferring a gram-molecule of metal from the electrode to the solution may be calculated in the same way as on p. 246, where we calculated it when salt passed from a dilute to a concentrated solution. It will have the value $\int_P^{P_m} v dP$, where P is the osmotic pressure of the ions in the solution, and P_m the electrolytic solution pressure of the metal. If E_1 is the potential difference at the surface, the electrical work is $E_1 qy$, where q is the electric transfer corresponding to the solution of a gram-equivalent, and y the valency of the ions. Thus as before,

$$E_1 qy = -\int_P^{P_m} v dP.$$

It is usual to go further, and make the assumption that both in the solution and in the metal the osmotic pressure obeys the gaseous laws. If this be done, we get equations (47) to (50) p. 247, in order of increasing inaccuracy, r being now unity.

So far we have been considering the solution of metal at the anode. In a Daniell cell, which we may take as example, there are three junctions to be considered, two metal-liquid, and one liquid-liquid. The effect on the electromotive force of the surface of contact of the two solutions will be considered in the chapter on the diffusion of electrolytes; it is very small compared with the potential differences at the surfaces of the two metals, and may here be neglected. On the assumption explained above, we may apply the logarithmic formulae to

the two metal-liquid junctions and express the electromotive force of the cell with the usual notation as

$$E = \frac{nRT}{qy}\left(\log \frac{P_{m_1}}{P_1} - \log \frac{P_{m_2}}{P_2}\right).$$

If we write the expression for the potential difference at one of these junctions in the form

$$\frac{nRT}{qy} \log P_m - \frac{nRT}{qy} \log P,$$

we see that $\frac{nRT}{qy} \log P_m$, which includes the so-called electrolytic solution pressure, is a mere constant for the metal at the given temperature. Writing this as M_1 we eliminate some of the assumptions of the preceding investigation, and apply the gaseous laws to the solutions only. The expression for the electromotive force of a Daniell cell then becomes

$$E = M_1 - M_2 - \frac{nRT}{qy}(\log P_1 - \log P_2)$$

$$= M_1 - M_2 - \frac{nRT}{qy} \log \frac{P_1}{P_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (56).$$

This equation may be derived directly from the principles of energetics by observing that the electric work of the cell must be equivalent to the algebraic sum of the following terms: (1) the work done in dissolving an equivalent of zinc from the electrode, its ions being produced at a standard pressure P_0; (2) the osmotic work $-\int_{P_0}^{P_1} vdP$ required to expand or compress the zinc ions so obtained; (3) the corresponding reversed work $+\int_{P_0}^{P_2} vdP$ required to reduce the copper ions to the standard pressure; (4) the work of depositing the copper on the cathode.

The equation shows that the electromotive force of a Daniell cell can be raised by diminishing the concentration of the zinc sulphate, or by increasing that of the copper sulphate. Since the third term in equation (56) is small compared with M_1 and M_2, this effect is slight.

We shall return to the consideration of the electrolytic solution pressure of the metals in the next chapter, under the head of single potential differences.

Oxidation and reduction cells.

In the chemical processes of oxidation and reduction, there occur changes in the valency of the ions, indicating changes in their electric charges. The energy of these processes can be made to supply an electric current. For example, two platinized platinum plates may be placed, one in a solution of stannous chloride, and the other in a solution of ferric chloride[1]. If the two be metallically connected, a current passes within the cell from the tin solution to that of the iron, stannic and ferrous chlorides being formed. The divalent stannous ion, taking up a third positive electric unit from the anode, becomes a trivalent stannic ion, while the equivalent amount of positive electricity is removed at the cathode by the conversion of the trivalent ferric into the divalent ferrous ion.

The gas cells with hydrogen and oxygen, or hydrogen and chlorine, as electrodes, may be classified in this group, the hydrogen being "oxidized" by its conversion into positively electrified hydrogen ions; in fact it is possible to regard all chemical cells from this point of view.

Transition cells.

Assuming that the cell may be treated simply as a reversible heat engine, Gibbs has deduced another expression for the electromotive force[2]. Let θ_1 be the transition point, the temperature at which the chemical action which gives rise to the current would go on reversibly in either direction, and let λ be the heat of reaction per electrochemical unit of mass if carried on outside the cell. Let θ be the temperature of the cell. Now λ heat-units at θ_1 are equivalent to $\lambda \frac{\theta}{\theta_1}$ units of heat at θ, together with $\lambda \frac{\theta_1 - \theta}{\theta_1}$ units of external work, as is indicated by the formula for the efficiency of a reversible engine. Thus for each unit of electricity which passes, a reversible cell being of maximum efficiency yields $\lambda \frac{\theta_1 - \theta}{\theta_1}$ units of electrical work, and $\lambda \frac{\theta}{\theta_1}$ units of reversible heat. Looked at in this way, the reversible evolution of heat is seen to be of the essence of the problem.

[1] See Le Blanc's *Electrochemistry*, Eng. Trans. p. 235.

[2] *B. A. Report* (1886), 388.

Now, as we know, the available electrical work, when one unit of electricity passes, measures the electromotive force, so that

$$E = \lambda \frac{\theta_1 - \theta}{\theta_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (57).$$

This result of Gibbs' is of great interest, for if two of the quantities λ, θ_1, and θ be known, the third can be calculated. Cohen[1] has verified the equation experimentally, and used it as a means of determining transition temperatures, obtaining values which agree well with those found in other ways or by direct observation.

Differentiating the equation with respect to θ, we get, since θ_1 is constant,

$$\frac{dE}{d\theta} = -\frac{\lambda}{\theta_1};$$

eliminating θ_1 by means of the equation (57) this gives

$$\frac{dE}{d\theta} = \frac{E - \lambda}{\theta}$$

or

$$E = \lambda + \theta \frac{dE}{d\theta}.$$

Thus we recover von Helmholtz's equation.

Returning to equation (57), we see that at the transition point, where θ becomes θ_1, the electromotive force vanishes. On this fact depends one of the methods used by Cohen[2] for determining transition points. Let us take, as an example, the case of the two hydrates of zinc sulphate, $ZnSO_4 . 7H_2O$ and $ZnSO_4 . 6H_2O$. Two vessels are filled with powdered zinc sulphate moistened with water, and connected by means of a tube filled with cotton-wool saturated with a solution of zinc sulphate. The vessels contain electrodes of zinc and are finally sealed up. The contents of one of them are now converted into $ZnSO_4 . 6H_2O$ by heating it for an hour to a temperature higher than the transition point. The whole cell is then placed in a thermostat, and connected in series with a galvanometer,

[1] *Zeits. phys. Chem.* XIV. 53 and 535 (1894).

[2] *Zeits. phys. Chem.* XIV. 53 and 544 (1894), or see Van 't Hoff, *Studies in Chemical Dynamics*, Eng. Trans. p. 193.

which is deflected, since the saturated solutions, in contact with different solids, are of different concentrations. The temperature is lowered and then allowed to rise slowly. The deflection falls, and finally is reversed, the exact point at which it vanishes being the transition temperature from the higher to the lower hydrate. When the temperature is maintained above the transition point for some time, the meta-stable form of salt passes completely into the stable form, the solutions become identical and the electromotive force gradually sinks to zero.

When a salt, for instance sodium sulphate, the metal of which cannot be used as an electrode, is to be examined, an electrode such as mercury in mercurous sulphate, which is unpolarizable with respect to the anion, is used.

Another method of determining transition points electrically by the use of a concentration cell is of special value when the meta-stable form of a substance is difficult to keep for any length of time. The electromotive force of a concentration cell depends, as we have seen, on the difference in concentration of the two solutions. Thus, if one solution be kept at a constant strength, and the other be kept saturated with salt, as the temperature slowly rises, any change in the solubility is shown by a corresponding change in the electromotive force. Now, as we saw on p. 40, the temperature-solubility curves for the two phases of a component cut each other at an angle at the transition point; so, although the solubility itself suffers no sudden change there, its temperature coefficient does. The temperature coefficient of the electromotive force, therefore, will also show a sudden change at the transition point, and the temperature-electromotive force diagram will consist of two branches, cutting each other at a sharp angle at that temperature. The cell is made up in open vessels, the solutions being kept stirred in order to insure the constant saturation of the one that is in contact with the solid. The diagram in Fig. 57 shows the electromotive forces of saturated sodium sulphate combined in a concentration cell with normal, half normal and quarter normal solutions, the weaker solutions giving the higher electromotive forces. The transition points estimated from these three cells are 33°·8,

33°·0 and 32°·9, the value found by other methods averaging about 33°. The theory of this second form of transition cell

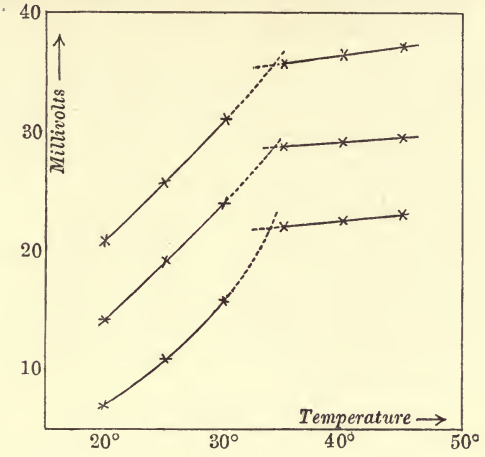


Fig. 57.

has been considered by Van 't Hoff, Cohen and Bredig[1], who show that the electromotive force can be calculated from the equation by using the known value of the heat of inversion.

This change in the direction of the solubility curve at the transition point, it will now be clear, affects the temperature coefficient of standard cells like that of Latimer Clark, which contain a saturated solution of zinc sulphate[2]. The transition point from $ZnSO_4.7H_2O$ to $ZnSO_4.6H_2O$ is 39°, and at this temperature there is a sudden change in the temperature coefficient of the electromotive force. When using the cell as a standard, a knowledge of the temperature coefficient is needed, and the cell would be unsatisfactory above 39°. The Weston cell, another standard, of the form

cadmium / saturated cadmium sulphate
/ mercurous sulphate / mercury,

has been recommended as having a much lower temperature coefficient than the Clark, and an electromotive force of approximately one volt (1·019). It has been shown, however, by

[1] *Zeits. phys. Chem.* XVI. 453 (1895).

[2] Barnes, *Jour. phys. Chem.* IV. 1 (1900).

solubility measurements[1], and by using the Weston as an inversion cell[2], that cadmium sulphate has an inversion point at 15°, which seriously interferes with its trustworthiness as a standard of electromotive force.

Irreversible cells.

Many of the cells in common use are essentially irreversible, and it is necessary to enquire how far the principles we have used for investigating the theory of reversible cells may be extended to others.

It has sometimes been held that irreversible cells have no definite electromotive force[3], the measured value depending among other things on the number of the ions of the metals used as electrodes which happen to be present in the liquids. On the other hand it may be argued that single-liquid polarizable cells of the type

zinc / potassium sulphate / copper,

are limiting cases of Daniell cells[4]. In accordance with the expression for the electromotive force of Daniell cells given on p. 257, namely

$$E = M_1 - M_2 - \frac{nRT}{qy} \log \frac{P_1}{P_2},$$

the electromotive force is independent of the absolute osmotic pressures of the two solutions; it will therefore be unchanged if the solutions be equally diluted. Now the remarks on p. 255 make it probable that the electromotive force is unaffected by the presence of a salt not containing the electrode metal, and if so, dilution with potassium sulphate solution will be equivalent to dilution with water. On this view, the initial electromotive force of the potassium sulphate cell, before polarization sensibly intervenes, should be equal to that of a Daniell, and a similar result should hold for other such cells. The errors of experiment on polarizable cells are considerable, but, as an ideal limit, the general results seem to be consistent with the required equality.

[1] Kohnstamm and Cohen, *Wied. Ann.* LXV. 344 (1898).

[2] Barnes, *Jour. phys. Chem.* IV. 339 (1900).

[3] Ostwald, *Lehrbuch*, II. 815.

[4] Bancroft, *Zeits. phys. Chem.* XII. 289 (1893); *Phys. Rev.* III. 250 (1896); Taylor, *Jour. phys. Chem.* I. 1 (1896).

Secondary cells or accumulators.

Any reversible cell can theoretically be employed as an accumulator, though in practice, conditions of general convenience are more sought after than strict thermodynamic reversibility.

The accumulator commonly used can be made by placing two lead plates in dilute sulphuric acid and passing a current between them. Hydrogen is evolved at the cathode, while the anode becomes covered with a layer of insoluble lead peroxide. As long as the metallic lead of the anode is in contact with the solution, it has been shown by C. J. Reed[1] that hydrogen is evolved at the cathode under a total electromotive force of about 0·5 volt, and a considerable volume of the gas can be collected if the area of the anode is large. Eventually the voltage necessary for the generation of hydrogen rises to about 2·3. This suggests that the first action at the anode is the formation of a coating of insoluble lead sulphate, which becomes the effective electrode and yields sulphuric acid and lead peroxide on further action of the current. The cell is now in a condition to give a current in the reverse direction, during which process lead sulphate is formed at both electrodes until these become identical in constitution. In a second charging, the lead sulphate at the cathode is reduced to spongy lead, while at the anode it again gives peroxide as before. Not even at the beginning of the second charging is the anode a lead electrode, and there is no action until the voltage reaches about 2·3. The mass of spongy material at the electrodes is increased by continual charging and discharging, which adds to the effective capacity of the cell; and the whole preliminary process of forming the cell can be greatly hastened if the plates receive in the first place a coating of red lead, Pb_2O_3.

The main chemical action of a fully formed accumulator seems to be in accordance with the equation

$$PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O,$$

which read from left to right describes the discharge, and from right to left the charging of the cell. Although ozone, hydrogen peroxide, persulphuric acid, and traces of lead persulphate have been detected, it seems likely that the above

[1] *Jour. phys. Chem.* v. 1 (1901).

equation represents the chief part of the changes. The concentration of the acid solution is an important factor in determining the electromotive force, which increases with increasing concentration, since part of the available energy of the reaction is due to the dilution of the residual acid by the water formed.

It is found in practice that the effective electromotive force of a secondary battery is less than that required to charge it; the energy efficiency of a lead accumulator is from 75 to 85 per cent., although from 94 to 97 per cent. of the current used in charging it can be regained. This drop in the electromotive force has led to the belief that thermodynamically the cell is only partly reversible. Dolezalek[1] however has attributed the discrepancy to mechanical hindrances, which prevent the equalization of acid concentration in the neighbourhood of the electrodes, rather than to any essentially irreversible chemical action.

On the provisional hypothesis that the system may be treated as reversible, the Gibbs-Helmholtz equation

$$E = \lambda + \frac{dE}{d\theta}$$

has been applied. The discharge reaction for dilute solutions gives a calorimetric heat-evolution of 87,000 calories, which, on the assumption that the energy is all available, is equivalent to an electromotive force of about 1·88 volts. This number agrees with that observed for cells filled with weak acid, and indicates that the temperature coefficient is very small, a result which has been experimentally confirmed by Streintz[2]. The quantitative measurements, by the same observer, of $dE/d\theta$ for different concentrations of the acid, can be used to calculate the increase of electromotive force for a given change in the concentration. Dolezalek calculates the same increase from the vapour pressure method applied by von Helmholtz to concentration cells. To accomplish this we must imagine two lead accumulators, one cell A containing more concentrated acid than the other cell B. Let them be arranged to work in opposite directions. Since the electromotive force of A is greater than that of B, the combination acts as a double cell and will produce a current in the direction natural to A. The

[1] *Zeits. Elektrochem.* IV. 349 (1898). [2] *Wied. Ann.* XLVI. 454 (1892).

chemical changes of the lead and its compounds are equal and opposite in the two cells, and the effective reaction consists in the transfer of two molecules of sulphuric acid from A to B while two molecules of water pass from B to A. The acid contents of the two cells thus tend to equality, and the double arrangement may be looked on as a concentration cell. The available energy is the difference between the work of mixture of pure sulphuric acid with water in the proportions of A and of B. This work can in either case be calculated if we imagine water distilled from the cell to the acid till the resulting liquid has the same composition as that in the cell, when it can be added to the cell without change of energy. Let p_1 and p_2 denote the constant vapour pressures of water, from the liquids in A and B respectively, and p the variable pressure over the isolated acid. The work of distillation from the cell A to the acid is $\int_p^{p_1} v\,dp$ (p. 242), or, if we assume that the vapour conforms to the gaseous laws, $RT \log \frac{p_1}{p}$ per gram-molecule, and for n_1 gram-molecules of water $RT \int_0^{n_1} \log \frac{p_1}{p}\,dn$. Thus the work of transferring one gram-molecule of H_2SO_4 from A to B is

$$W_2 - W_1 = RT \int_0^{n_2} \log \frac{p_2}{p}\,dn - RT \int_0^{n_1} \log \frac{p_1}{p}\,dn$$

$$= RT \left(n_2 \log p_2 - n_1 \log p_1 - \int_{n_1}^{n_2} \log p\,dn \right).$$

The actual changes in the double cell also involve the transfer of one gram-molecule of water from B to A, a process which by distillation would involve the work $RT \log \frac{p_2}{p_1}$. Finally we have for the electromotive force of the double cell

$$\delta E = RT \left(n_2 \log p_2 - n_1 \log p_1 + \log \frac{p_2}{p_1} - \int_{n_1}^{n_2} \log p\,dn \right).$$

The vapour pressures of sulphuric acid of various concentrations have recently been measured accurately by Dieterici[1], and from his results the above equation can be solved numerically. Dolezalek has measured the electromotive force E of lead cells in ice, as follows :

[1] *Wied. Ann.* L. 61 (1893).

Cell	E	Density of acid	% H_2SO_4	Grams of water to 1 grm.-mol. H_2SO_4	Vapour pressure in mm. Hg
I	2·29	1·496	58·37	69·88	0·796
II	2·18	1·415	50·73	95·16	1·438
III	2·05	1·279	35·82	175·58	2·900
IV	1·94	1·140	19·07	415·8	4·150
V	1·82	1·028	3·91	2408·4	4·574

The differences between these observed values of the electromotive force were compared with the results of theory in two ways: by the vapour pressure equation deduced above, and by the use of von Helmholtz's equation combined with a knowledge of the heat of dilution of sulphuric acid. As measured by Thomsen, this heat of dilution may be expressed as

$$H = \frac{ab}{b + 1{\cdot}798a}\, 17860 \text{ calories}$$

when a gram-molecules of sulphuric acid are mixed with b gram-molecules of water. The results of the comparison are given in the following table.

Double cell	δE			
	Calculated		Observed	
	From H	From p	Dolezalek	Streintz
I—V	0·40	0·45	0·47	—
I—IV	0·29	0·34	0·35	—
II—IV	0·22	0·25	0·24	—
II—V	0·32	0·37	0·36	—
III—V	0·22	0·22	0·23	0·23
III—IV	0·11	0·12	0·11	0·13
II—III	0·11	0·13	0·13	0·15
I—II	0·08	0·08	0·11	—
IV—V	0·11	0·10	0·12	0·11

The agreement of these numbers not only confirms the theory given, but also indicates the general conformity of the lead accumulator to the thermodynamic properties of reversible systems.

CHAPTER XI.

CONTACT ELECTRICITY AND POLARIZATION.

Volta's contact effect. Thermo-electricity. The theory of electrons. Single potential differences at the junctions of metals with electrolytes. Dropping electrodes. Electrocapillary phenomena. The theory of von Helmholtz. Electric endosmose. Single potential differences (continued). Electrolytic solution-pressure. Electrochemical series. Polarization. Decomposition voltage. Polarization at each electrode. Evolution of gases. Electrolytic separations.

Volta's contact effect.

THE source of the energy of a galvanic cell is certainly the chemical action, a correction being applied for any reversible heat which the cell absorbs from or gives up to its surroundings. The exact seat of the difference of potential, however, has remained undetermined for a century, and proved a fruitful subject of discussion. Volta located it at the junction of the unlike metals; while Faraday's work, which showed the regular and fundamental part played by the chemical processes, seemed to indicate the surfaces at which the metals were in contact with the liquids. These two views of the nature of the phenomena have continued till the present[1], though it seems, from the evidence described in the last chapter and for other reasons that will be given, that a considerable difference of potential probably exists at the surface of separation between metals and electrolytes or

[1] For a description of the phenomena of the contact effect, and an account of the Volta theory, see Lord Kelvin, *Phil. Mag.* July, 1898. For the other point of view, see Sir Oliver Lodge, *Proc. Phys. Soc. Lond.* XVII. 369 (1900); and *Phil. Mag.* XLIX. 351 and 454 (1900).

dielectrics such as air. The facts to be explained, besides those of the galvanic cell, are as follows.

Dry zinc and copper brought into contact with each other in dry air become oppositely charged, and, if their surfaces are arranged parallel and very close to each other, so as to form a condenser of large capacity, these charges may be considerable. They can be exhibited by separating the plates; the capacity is then diminished and the difference of potential is thereby increased, so that it can be indicated by an electroscope or measured by an electrometer. By making the connexion between the metals through part of a potentiometer, a difference of potential in the direction opposite to that natural to the junction can be applied. Adjusting the potentiometer till, on separating the plates, the electrometer is not deflected, the natural potential difference can be determined. Another method consists in making the actual quadrants of an electrometer of the two metals to be examined. On connecting them through a wire a deflection is observed which can be destroyed by applying an external electromotive force in the opposite direction. An electromotive force of about three quarters of a volt neutralizes the natural potential difference produced by the contact of zinc and copper.

Many experiments have been made on this subject; to some of them we shall refer below. Ayrton and Perry have examined many metals, obtaining among others the following potential differences in volts[1].

Zinc, Lead	0·210
Lead, Tin	0·069
Tin, Iron	0·313
Iron, Copper	0·146
Copper, Platinum	0·238
Platinum, Carbon	0·113

By the summation of potential differences, a principle experimentally established by Volta, we can find the contact effect between any two metals in this list by adding together the values for all the pairs of intervening metals.

[1] *Phil. Trans.* CLXXI. 15 (1880).

It will be noticed that in all the phenomena described it is the difference of potential in the air surrounding the two metals which is experimentally observed. Nevertheless, many physicists, following Volta, have held that this potential difference in the air is due to, and measures, a natural potential difference between the metals themselves. When the metals are surrounded, except at the area of contact, with the non-conductor air, this potential difference is maintained, and can be demonstrated by means of an electrometer. In a galvanic cell it is supposed that the metallic contact between the electrodes constantly keeps up a potential difference, which is constantly tending to sink to zero by the action of the electrolytic liquid.

The theory of the cell given in the last chapter suggests that the chief potential difference is to be sought at the liquid-metal surface; but it is clear that, before any such interpretation can be accepted, it must be reconciled with the phenomena of contact electricity just described. On the analogy of the cell, the most natural explanation is that the potential difference is due to the action of the oxygen of the air; and this hypothesis receives support from the possibility of approximately calculating the observed Volta force as the electrical equivalent of the difference between the heats of oxidation of zinc and copper. It is perhaps not necessary to imagine actual oxidation; a sufficient cause might possibly be found in some slight modification of the film of condensed gas, which, as we have seen, seems to exist on all solid surfaces, and to be so difficult to remove.

The chemical affinity of the oxygen for the zinc can be represented by supposing the film of gas to be electrically polarized, perhaps by the similar orientation of the electrically bipolar oxygen molecules. Such polarization would produce a layer of oxygen atoms straining to attack the zinc but prevented from reaching it by want of a way of escape for the corresponding negative charge from the metal, or of a means of approach for an equivalent positive charge. Another metal such as copper will have a different affinity for oxygen, and thus the electrical potential difference between it and the surrounding air will be different from that shown by zinc. If contact be made between

them, the potentials of the metals are equalized, or at any rate reduced to the small difference of true metallic contact, by a flow of electricity, which, looked at in another way, may be referred to the greater force of attraction for oxygen shown by the zinc than the copper. Modifying double electric layers are thus produced at each interface, analogous to those caused by electrolytic polarization. This process may perhaps be accompanied by incipient chemical combination between positively electrified zinc atoms at the surface of the metal and negatively electrified oxygen atoms in the film of air. The corresponding positive atoms of oxygen would then no longer be neutralized, and would give the film of air and its neighbourhood a positive potential. The zinc and copper themselves are at the same potential, but since the outside of the condensed film on the zinc is more intensely positive than that on the copper, there is a potential gradient through the air between them. It is this difference of potential that is observed in experiments on contact electricity.

A modification of the above hypothesis has been suggested by Lodge, who imagines that, when contact is made between the metals, the negative atoms of the oxygen film facing the zinc move nearer to the metal, while the film outside the copper recedes further from it. A change is thus produced in the thickness of the two condensers formed by the zinc-oxygen and the copper-oxygen layers. Their capacities are altered in opposite senses, and an electric transfer must take place from one to the other. Now the capacities must be large, since the separating space is of molecular dimensions, and Lodge has shown that a change of about the hundred thousandth of the original thickness will produce enough electric transfer to give the observed charges to the parallel metal plates, which form a condenser of relatively enormous thickness, and hence of very small capacity.

In passing from either metal to the surrounding air, there is a sudden rise of potential, but this rise is greater for the zinc than for the copper. We can calculate the magnitude of each step of potential on the assumption that all the heat of oxidation passes into the energy of electrical contact, and that the method

of calculating the electromotive force of a cell, given on pp. 235, 237, is applicable to each electrode considered separately. If oxygen were removed by the metal from the film of air, its place would be supplied from the free atmosphere, so that the effective process which is possible is the oxidation of zinc by gaseous oxygen; it is therefore the ordinary heat of oxidation that is involved. The value of this heat for a gram-molecule of zinc is about 85,800 calories, and for copper about 37,200 calories. For the electrochemical equivalents, the mechanical values correspond to 1·85 and 0·80 volt. We can experimentally determine only the difference of these effects. Observation indicates about 0·7 or 0·8 volt, which is appreciably less than the calculated result.

When, instead of the insulator air, the plates are surrounded by an electrolytic conductor, the slope of potential is accompanied by a current through the solution. At the contacts of the liquid with the metals, the natural potential difference is constantly tending to be again set up by the chemical affinity; thus a constant current is maintained and zinc is actually dissolved.

The probability that the contact effect depends on the chemical action or affinity of the surrounding medium will be much increased if it can be shown that the magnitude of the effect depends on the nature of the medium. Many experiments, such as those of Bottomley, indicate that no change is produced by working in vessels at high exhaustion, or by placing the metals in an atmosphere of hydrogen, though a reversal of the sign of the potential difference was obtained by J. Brown by replacing the air by hydrogen sulphide or ammonia[1]. The film of gas which clings to a solid is exceedingly difficult to remove, and it now seems likely that its persistence explains the negative results so often found. From a recent research by Spiers[2], in which extraordinary precautions were taken to remove the film of gas, it is clear that the difficulties of getting rid of it have been greatly undervalued, and that, when it is really disturbed, large changes in the

[1] *Proc. R. S.* XLI. 294 (1887).

[2] *Phil. Mag.* XLIX. 70 (1900).

magnitude of the Volta force are produced. More work on this point is very desirable, but in such a case, a few experiments that yield a positive result, and indicate a probable reason for the negative results of others, seem to carry great weight. The effect of small changes in the nature and condition of the surfaces has been recently studied by Erskine-Murray[1], who showed that the potential was increased by polishing and burnishing, and diminished by a film of oxide. There would certainly be less affinity between gas and a partially oxidized metal than between gas and a clean metal, and we should naturally expect the potential difference to be reduced by oxidation.

Thermo-electricity.

The phenomena of thermo-electricity have an intimate connexion with the subject now under consideration[2]. Let us imagine a condenser composed of two plates of different metals, separated by a layer of dielectric and connected by means of a wire of a third metal. In applying the principles of thermodynamics to this system, there are two irreversible processes to be considered; the conduction of heat along the metals, and the frictional generation of heat by the flow of the current. The latter effect, being proportional to the square of the current, will be negligible when the current is very small, and can therefore be considered to be eliminated under ideal conditions. The conduction of heat may be neglected if it proceeds independently of the current, except for the reversible Thomson effect considered below; this independence it is necessary to assume.

In order to explain the phenomena of the reversal of thermo-electric currents when one of the junctions of certain metallic circuits continually rises in temperature, Lord Kelvin has imagined a convection of heat by the passage of the current. Thus the heat absorption per unit quantity of electricity may be written as $\sigma\delta T$ for a current passing up the temperature-gradient, where σ may be called the specific heat of electricity,

[1] *Phil. Mag.* XLV. 398 (1898).

[2] See for instance, Larmor, *Aether and Matter*, p. 306.

and denotes possibly a differential effect, depending on an inequality in the properties of streams of oppositely moving ions. The corresponding heat absorption for a second metal may be expressed as $\sigma' \delta T$.

Now let us consider a complete circuit of these two metals, T_1 and T_2 being the temperatures of the junctions. Let Π_1 and Π_2 be the heat evolved by unit electric transfer at the junctions of the temperatures T_1 and T_2 respectively; Π_1 and Π_2 are called the Peltier effects. Then, considering unit electric transfer round the circuit, the energy and entropy principles lead to the results

$$E = \Pi_1 - \Pi_2 + \int_{T_1}^{T_2} (\sigma - \sigma')\, dT \ldots\ldots\ldots\ldots (58),$$

and

$$\frac{\Pi_1}{T_1} - \frac{\Pi_2}{T_2} + \int_{T_1}^{T_2} \left(\frac{\sigma}{T} - \frac{\sigma'}{T}\right) dT = 0 \ldots\ldots\ldots\ldots (59).$$

By differentiation, equation (59) gives

$$\frac{d}{dT}\left(\frac{\Pi}{T}\right) + \frac{\sigma - \sigma'}{T} = 0,$$

whence we obtain

$$E = \int_{T_1}^{T_2} \frac{\Pi}{T}\, dT,$$

or

$$\frac{\Pi}{T} = \frac{dE}{dT}.$$

Thus, while the Peltier effects depend on the temperature coefficient of the total electromotive force of the circuit, in equation (58) for E, the Peltier effect appears as a local electromotive force at the junction. Each electron as it passes across, introduces an energy effect $q\Pi$ which involves a reversible evolution or absorption of heat. The Peltier effects have been experimentally determined, and their electrical equivalents, which measure the contact potential differences at the metallic junctions, are calculated as a few millivolts only, values much too small to explain by themselves the observed Volta effects, without taking account of similar effects at the surfaces of the surrounding dielectric.

The theory of electrons.

According to the corpuscular theory of electric conduction, the passage of a current through a metal is accompanied by the transfer of electrons in its line of flow. In each metal, the corpuscles or electrons are present in a certain concentration on which depends the conductivity of the material, and may perhaps produce something of the nature of osmotic pressure. On the analogy of Nernst's conception of electrolytic solution pressure at the junctions of metals and electrolytes, a similar characteristic pressure has been imagined at the surface of one metal in contact with another. The better conducting metal in which the corpuscles are more concentrated, will send electrons into the other metal till the equilibrium of the various tendencies prevents further transfer. The electrostatic effect thus produced is the explanation on this view of the potential difference of contact.

We may thus imagine two metals in contact to be in a certain sense a concentration cell, the difference of concentration being that of the electric corpuscles in the two materials. On this view, the contact potential difference is analogous to the electromotive force of the cells previously described. There is however a vital difference between the two cases. A concentration cell is a system in an unstable state; if a current passes through it, the difference of concentration is changed, and the electromotive force altered. Two metals in contact, on the other hand, possess a constant difference of corpuscular concentration, which must re-establish itself if disturbed. In this case, then, there is no source of energy available for the production of a current; and, consistently with this result, the total electromotive force of a circuit of several metals at the same temperature is found to vanish. Nevertheless, if we accept the idea of corpuscular osmotic pressure, the transfer of corpuscles from one side to the other of a metallic interface will involve the loss or gain of osmotic work. The energy change thus produced may be but another aspect of the contact difference of electrical potential; it may be a complicating effect, which will alter the relation of that potential difference to the Peltier effect of reversible heat production.

Single potential differences at the junctions of metals with electrolytes.

Many attempts have been made to determine experimentally the single potential differences at the individual junctions in a circuit containing electrolytes as well as metals. In a galvanic cell, for example, there must be at least two such junctions, and the problem is to separate their effects and measure the step of potential at each. The measured electromotive force gives the sum of all the single potential differences, but the impossibility of directly connecting the electrolyte with an electrometer without introducing another metallic junction throws difficulties in the way of observing them individually. If a method could be devised capable of application to one such junction, the combination of that junction with any other would enable the value for the other to be calculated from the total electromotive force as observed in the usual manner.

Two possible diagrams of the distribution of potential in a simple galvanic circuit are exhibited in Fig. 58. The diagrams are supposed to be drawn completely round the surface of a

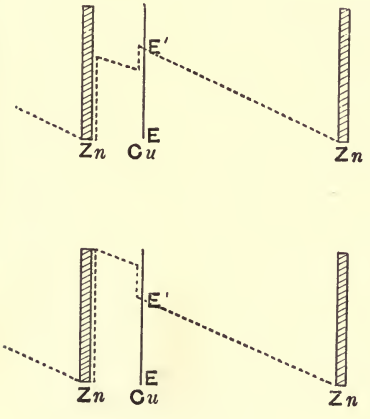


Fig. 58.

Fig. 59.

cylinder and then unrolled, so that the two vertical lines marked *Zn* denote the same zinc plate, considered to be at the zero of potential. Beginning at the left end of the figure, there is a sudden rise of potential at the surface of the zinc, the

potential difference of the electric double layer being denoted by the vertical rise of the dotted line. Passing through the cell there is a downward potential gradient due to its resistance to the current. At the surface of the copper plate, there is another discontinuity of potential, upwards or downwards according as the natural potential difference at the copper-electrolyte surface has a sign opposite to or the same as the zinc-electrolyte junction. These two possibilities are indicated in the two diagrams of the figure; the external electromotive force of the cell, the same in each case, being represented by the vertical height EE'. Since both metals are oxidizable, though not with the same readiness, we should expect the potential difference with the liquid to have the same sign for copper as for zinc, though generally received experiments described below indicate opposite signs. Leaving the copper plate, there is another potential gradient conforming to Ohm's law in the external circuit, till, at the outside surface of the zinc, the potential again falls to zero. If the external circuit be broken, the natural potential differences at the surfaces of contact remain unaltered, but the Ohmic potential gradients are destroyed. The resulting diagrams are shown in Fig. 59, in which EE' now denotes the total electromotive force of the cell, as measured on open circuit. Thus it will be seen that a determination of the electromotive force of the cell only tells the value of EE', the algebraic sum of two effects. The absolute values of these two effects remain undetermined; it is even uncertain whether they have the same or opposite signs. Since the current passes from metal to electrolyte at the surface of the zinc, and from electrolyte to metal at the surface of the copper, both junctions help to drive the current if the signs of the two effects are different, while, if the signs are the same, the copper plate reduces the natural electromotive force of the zinc electrode.

For circuits containing metals and dielectrics only, Volta's law of the summation of potential differences is a necessary consequence of the principle of the impossibility of perpetual motion, but if electrolytes connect the metals, the possible chemical action gives a source of energy, and Volta's law cannot be assumed to hold good without experimental demonstration.

Again, the potential difference between copper and zinc in air is probably due to the more or less complete transverse orientation of bipolar molecules at the metal / air interfaces, but for a metal / electrolyte junction, besides the corresponding molecular orientation, due to the essential difference in the nature of the two materials, there is a superposed potential difference due to the presence of a double sheet of electrolytic ions in the neighbourhood of the surface. If a small external electromotive force be applied across the junction in the direction opposite to that of the natural potential difference, the number of ions in the double layer is altered, and, by proper adjustments, the ionic effect might be destroyed. The natural potential difference, due to the molecular orientation, however, will probably not sensibly be affected. On the other hand, when a current flows, chemical changes occur, and the molecular layer may in time be disturbed. The electromotive force of a galvanic cell may possibly involve the potential differences due to the molecular arrangement at the various junctions, as well as those due to the distribution of ions. It seems probable, however, that the methods commonly used for determining single potential differences at the junctions of metals and electrolytes give the differences due to the ionic layers only. If so, before the experimental methods can be considered to solve the problem of the location of the effective potential differences in a galvanic cell, it is necessary to prove that Volta's summation law holds with regard to the molecular potential differences, so that its total effect in the circuit vanishes.

We must now pass to the consideration of the attempts that have been made to determine these single potential differences. The results are still doubtful and unsatisfactory, but, nevertheless, a somewhat full account of the subject will be given, for it has produced much experimental investigation, and further light is greatly to be desired.

It is generally believed that the single potential difference at the common boundary of mercury and an electrolyte has been satisfactorily determined by experiments on capillary electrometers and by others in which mercury was allowed to drop into a solution. Nevertheless, uncertainties arise in the

interpretation of the phenomena, and doubt may well be felt about the results deduced. Another method of investigation has been adopted by Exner and Tuma, and by Exner[1], and although it is open to criticism we will first briefly consider it as it illustrates the difficulties inherent in the subject.

Dropping electrodes.

The introduction of the dropping electrode is due to Lord Kelvin, and was applied by him to determine the difference of potential between the earth and any point in the atmosphere. If a conductor is constantly giving off a stream of particles into the surrounding dielectric medium which is at a potential different from that of the conductor, each particle carries away an electric charge until the potential of the conductor is made equal to that of the conducting boundary of the insulator if the latter is itself unelectrified. By connecting the conductor with an electrometer, the potential of the dielectric at the point of emission of the particles is determined. The particles may be drops of water or mercury, the products of combustion of a flame, or the smoke from a slow-burning match. For measuring the high voltages observed in meteorology, any of these arrangements are trustworthy, but when the differences of potential to be observed are one volt or less, the conductivity due to combustion restricts the method to the use of some kind of drop.

In examining the junction of a metal with an electrolyte, Exner connected the metal to earth and to one quadrant of the electrometer, while the electrolyte was joined by means of a thread moistened with the same solution to a cylinder of filter paper also soaked in the liquid. The cylinder forms a virtually closed conductor, and the inside of it is therefore an equipotential region, and is assumed to have the potential of the surrounding electrolyte. A funnel having a capillary end is filled with mercury which falls in drops starting within the cylinder. The stock of mercury in the funnel is connected with the other quadrants of the electrometer. In this way the mercury gradually assumes the potential of the air inside

[1] *Sitzungsber. Kais. Akad. Wien*, XCVII. 917 (1889); C. 607 (1891); CI. 627 and 1426 (1892).

the moistened cylinder, except for any natural difference of potential between the air and the falling drops of mercury, or any electrification produced by friction with the funnel, etc. In order to correct for these effects, Exner arranged a null experiment in which the mercury drops formed inside a cylinder of carbon or platinum connected with the earth, and the reading of the electrometer then obtained was taken as zero. Now in doing this, any natural difference of potential between platinum and air is neglected, and thus all the results of the work are in error by a constant amount which should be added to or subtracted from them. The error may be small, but there is no means of estimating its magnitude. Moreover, if there is any natural potential difference between the electrolyte and the air, it also is included in the numbers obtained; in fact, by the principle of the summation of electromotive forces, we see that, when electric transfer ceases, the total electromotive force of the circuit

mercury / air / solution / metal / air / metal / mercury

must vanish. To secure this result, the solution / metal interface is polarized by a double ionic layer; if the necessary double layer were too intense, there would presumably arise a continual leakage current, maintained by the energy of the falling drops.

Another form of application of Lord Kelvin's dropping electrodes furnishes one of the methods in common use, to which reference has already been made, for the examination of the electric phenomena at the junction of mercury with an electrolyte. Von Helmholtz pointed out that a potential difference at such a junction would be produced by a double layer of electricity over the surface, the two opposing faces being oppositely charged—on the side of the electrolyte by the congregation of ions as explained above. Such a system would take time to reach its final state, and he concluded that if mercury were allowed to drop rapidly from an orifice beneath the surface of a liquid electrolyte, the double layer would not be established, and the stock of falling mercury would be brought to the same potential as the electrolyte. The

apparatus might therefore be used in connexion with an electrometer as is the dropping electrode in meteorology, the other quadrants being joined to a quantity of mercury at rest in the same electrolyte. A difference of potential of about 0·8 or 0·9 volt is obtained between the dropping mercury and the mercury at rest in dilute sulphuric acid; but it has been pointed out by Exner and by Brown[1] that the result is complicated by the electromotive force of the cell composed of the mercury with the clean surface newly exposed by the drop as it forms, the electrolyte, and the mercury, tarnished or affected in some way by the action of the solution, which is at rest in the bottom of the vessel. This part of the observed electromotive force may depend on potential differences of the type due to the regular orientation of bipolar molecules. It would be set up almost instantaneously at the interface, and thus would not be eliminated by the action of the falling drops. Again, Warburg[2] has suggested that owing to the formation of mercury salts in electrolytic solutions containing dissolved oxygen, an explanation of the phenomenon might be found in the electromotive force of the concentration cell,

mercury / dilute mercury salt / concentrated mercury salt / mercury,

since differences of concentration at the electrodes will be produced by the passage of a current. It seems likely at all events that both these effects are involved in the current which will flow through a connecting wire from the standing to the falling mercury. In examining the results of researches on mercury dropping electrodes, these inherent difficulties should be borne in mind.

A third explanation of the dropping electrode is given by Nernst's theory of electrolytic solution pressure. The solution pressure of mercury is very low, and mercury ions tend to be deposited as metal on a mercury surface, even from a very dilute solution of one of its salts. As the drops form, mercury ions are absorbed by their newly exposed surfaces, and negative

[1] *Phil. Mag.* [5] xxvii. 384 (1889).
[2] *Wied. Ann.* xxxviii. 321 (1889).

ions are attracted to the ionic layer of the electrolyte next the interface. These negative ions are carried down with the drops as they fall; they enable mercury ions to redissolve in the lower parts of the solution when the drops coalesce with the standing mercury and the area of contact is diminished. This explanation involves a loss of mercury salt in the upper regions of the solution, and a corresponding gain below. Such changes of concentration have actually been observed by Palmaer by electrical and chemical methods in an unsaturated solution of calomel, through which mercury was allowed to drop[1].

Experiments have been made by different observers on electrodes dropping mercury directly into electrolytic solutions, with results that did not agree very well among themselves. If the orifice be within the electrolyte, the time of fall of the mercury as a continuous jet allows the ionic potential difference of the interface to partially establish itself, but Paschen[2], who investigated the subject in 1890, came to the conclusion that concordant values could be obtained by making the mercury jet emerge from the orifice into air, but break into drops just as it reached the surface of the electrolyte. His experiments on liquid amalgams, however, seemed to indicate that even in this way the mercury or amalgam is not completely deprived of its electric charge on entering the solution.

It is commonly assumed that in experiments on such mercury dropping electrodes the total potential difference between the falling mercury and the solution is destroyed. There are observations, however, by G. Meyer[3] and S. W. J. Smith[4] which make such an interpretation difficult to accept. We shall see later that, from a knowledge of the ionic mobilities, Nernst and Planck have calculated the rates of diffusion of electrolytes and hence the difference of potential between the solutions of two electrolytes in contact with each other. On their theory, and indeed on almost any possible view of the phenomena, there can be no potential difference between dilute

[1] *Zeits. phys. Chem.* XXV. 265 (1898); XXVIII. 257 (1899); XXXVI. 664 (1901).
[2] *Wied. Ann.* XLI. 42 (1890).
[3] *Wied. Ann.* LVI. 680 (1895).
[4] *Phil. Trans.* CXCIII. A (1900).

equivalent solutions of potassium chloride and iodide, which are ionized to the same extent, and contain ions possessing equal mobilities. The potential difference between either of these two solutions and a mercury dropping electrode should also vanish, and the electromotive force of the cell

dropping mercury / KCl / KI / dropping mercury

should be zero. Its observed electromotive force is given by Meyer as 0·284 and by Smith as 0·262 and 0·256 volt. This result apparently indicates that part of the potential difference at a mercury-electrolyte interface depends on the nature of the anion; it is not eliminated by the action of a dropping electrode, and is therefore probably established with much greater rapidity than the part of the potential difference which is so eliminated.

Electro-capillary phenomena.

The surface tension of the area of contact between the mercury and a solution is affected by its electrical state. If the surface be increased, an electric transfer is produced, and, conversely, if an external electromotive force be applied across the junction, the area tends to change, owing to an alteration in the effective surface tension. These phenomena have been applied by Lippmann[1] to the construction of capillary electrometers, of which several forms are in frequent use. In one variety, a vertical glass tube is drawn to a very fine capillary. The tube is partially filled with mercury, and the lower portion immersed in an electrolyte, usually dilute sulphuric acid, in which is placed another quantity of mercury. The capillary forces tend to raise the mercury surface in the little tube, and are balanced by the pressure of the long column. When the mercury in the vertical tube and

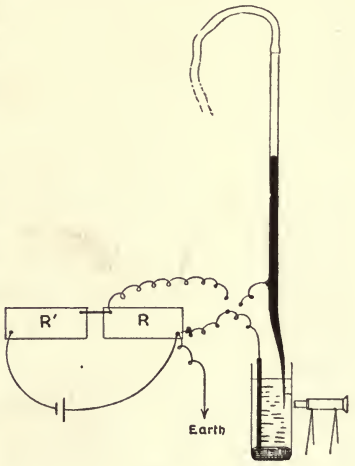


Fig. 60.

[1] *Pogg. Ann.* CXLIX. 561 (1873); *Ann. de Chim. Phys.* [5] v. 494 (1875).

the mercury below the electrolyte are connected with two conductors at different potentials, such as the opposite poles of a galvanic cell, a change is produced in the level of the surface of contact in the capillary tube. A microscope with a micrometer eyepiece may be arranged to view the capillary, and, for small differences, the change in level is found to be proportional to the applied difference of potential. The movement is slow, and the final position of the meniscus is not reached for an appreciable time, probably owing to the high values of the electrical resistance of the column of electrolyte in the capillary, and of the frictional resistance to the movement of liquid through such a narrow tube[1]. Burch[2] has shown that, while the applied electromotive force is a small fraction of a volt, the electrometer behaves as a condenser of good insulation, retaining its charge for several hours when disconnected from the cell. On the other hand, when the applied voltage is greater, electrolysis at the surface seems to occur, and the charges leak away. If, during the process of charging, the cell be disconnected before the final position of the meniscus is reached, the movement at once stops, and, in any case, the instrument is quite dead beat, and never oscillates about its position of equilibrium except as the result of mechanical disturbance.

The theory of von Helmholtz.

An explanation of these phenomena, based on Lippmann's observations, has been given by von Helmholtz[3], on the assumption that no electrolysis occurs. Any natural potential difference between two bodies implies an electrification over the boundary, in such a manner that an electric condenser of minute thickness is formed, with its parallel faces oppositely charged. This electric double layer will produce an electrostatic surface energy ϵ, the value of which is $\frac{1}{2}CA\Pi^2$, where C is the capacity of the double layer per unit surface, A the area of contact, and Π the potential difference across the layer. Now if Π be kept constant, and

[1] *Phil. Trans.* CLXXXIII. A, 104 (1892). [2] *Proc. R. S.* LXX. 221 (1902).

[3] *Wied. Ann.* XVI. 35 (1882), Faraday Lecture, *Chem. Soc. Jour.* (1882); see also Larmor, *Phil. Mag.* [5] XX. 422 (1885), and S. W. J. Smith, *loc. cit.*

the area be increased, we have for $d\epsilon/dA$ the value $\frac{1}{2}C\Pi^2$. This increase in available energy is obtained from the chemical energy which maintains the natural potential difference. The electric layer on either side of the interface tends to expand under the mutual repulsion of the different parts of its charge, and thus tends to increase the area of contact; it therefore acts in a sense opposite to that of the ordinary surface tension S_0. The total surface tension S will be

$$S = S_0 - \tfrac{1}{2}C\Pi^2.$$

On the assumption that the only effect of the potential difference is to produce such an electrostatic effect, S_0 will be independent of Π, and the total observed surface tension will reach a maximum when Π is zero. Nevertheless, it is possible that the potential difference may affect the nature of the surface chemically or otherwise, and thus change S_0 the ordinary surface tension. The maximum value of S will, in this case, not necessarily imply that the potential difference of the double layer is zero.

The usual methods, by which attempts have been made to determine the total natural potential difference between mercury and an electrolyte, really give, on the view advocated above, only the part of that total due to the ionic double layer. If we assume that the electrostatic effect is the only result of changing the ionic difference of potential by applying an external electromotive force, and that the analogy with the condenser still holds good, the natural ionic potential difference will be equal and opposite to that which must be applied externally in order to reach the maximum value of the observed surface tension. Lippmann and others have in fact found that the curves drawn between the external electromotive force and the reading of a capillary electrometer, are roughly parabolic; with dilute sulphuric acid, the maximum of the curve is reached when about one volt is applied. Conversely, when the surface of separation is stretched, a current flows to supply the charges for the increased area of the double layer of electricity, and Pellat[1] found that this current ceased

[1] *Comp. Rend.* CIV. 1099 (1887).

when an external electromotive force of 0·97 volt acted against the natural potential difference.

By using liquid amalgams, the same electrolyte can be compared with mercury and what is effectively a different metal. Rothmund[1] and others have compared the difference of the values thus measured with the electromotive force of the cell

amalgam / electrolyte / mercury,

finding concordant results.

Rothmund gives the following as the voltages required to give the maxima of surface-tension:

Mercury	in normal	sulphuric	acid solution	+0·926 volt
Mercury	„	hydrochloric	„ „	+0·560 „
Lead amalgam	„	sulphuric	„ „	+0·008 „
Bismuth	„ „	sulphuric	„ „	+0·478 „
Tin	„ „	hydrochloric	„ „	+0·080 „
Copper	„ „	sulphuric	„ „	+0·445 „
Cadmium	„ „	sulphuric	„ „	−0·079 „
Zinc	„ „	sulphuric	„ „	−0·587 „
Thallium	„ „	hydrochloric	„ „	+0·089 „

In the experiments with mercury, the acids were saturated with their mercurous salts, and when using amalgams a trace of the salt of the metal was added to the solution. Cells were then arranged with these amalgams in combination with the corresponding mercury electrodes.

	Observed E.M.F.	Calculated E.M.F.
Lead amalgam cell	0·923	0·918
Bismuth „ „	0·437	0·448
Tin „ „	0·534	0·480
Copper „ „	0·458	0·481
Cadmium „ „	1·090	1·005
Zinc „ „	1·472	1·513
Thallium „ „	0·652	0·471

The results of these experiments, unlike those on cells with dropping electrodes above described, on the whole favour the view that the electromotive force of a cell is the sum of the

[1] *Zeits. phys. Chem.* xv. 1 (1894).

single potential differences at its electrodes as determined by the capillary electrometer, and that any permanent part of the total potential differences due to the orientation of bipolar molecules is not involved.

On the other hand, there is evidence to show that in general the result of an applied electromotive force on the surface tension is not merely the electrostatic effect contemplated by the Helmholtz theory, but depends also on the chemical nature of the electrolyte.

The capillary electrometer may be imagined to consist of a very small condenser, composed of the mercury-electrolyte double layer in the capillary, arranged in series with a large condenser formed of the similar surface in the outer vessel. Such a small condenser will be charged by an electric transfer which does not appreciably affect the large one, and the variation of the potential difference at the capillary electrode is the same as the variation of the external electromotive force.

The Lippmann-Helmholtz theory rests on two hypotheses. It assumes that the electrometer circuit may in truth be treated as a system of condensers, and it assumes that, as explained above, the only effect of the potential difference, whether natural or applied, is the electrostatic one.

To increase the surface tension, and thus to reduce the natural electrification, of the interface between mercury and an electrolyte, an external electromotive force has to be applied from the solution to the metal. The natural ionic double layer must therefore consist of negative anions, chlorine for example, in the electrolyte, and a corresponding positive charge, perhaps represented by positive electrons, on the surface of the mercury. On applying a gradually increasing reverse electromotive force, we may imagine that the chlorine ions diminish in number and finally disappear; the surface tension then reaches a maximum. Beyond this point, positive metallic ions would be driven up to the interface, and a reverse double layer would arise. If this polarization exceeded a certain limit, a current would flow, and an amalgam might be formed. On the original Helmholtz theory, which took no account of differences between ions, and assumed that the reverse layer was similar to the first one, the

experimental voltage surface-tension curves should be a single parabola. Observation shows, however, that there is usually a slight want of symmetry between the ascending and descending branches of the curves, possibly indicating the effect of the chemical nature of the ions. The result of this effect on the surface energy of the interface has been considered by van Laar[1]. When an electric transfer δq occurs, the change in surface energy will be given by the expression

$$\delta\epsilon = \frac{\partial(SA)}{\partial q}\delta q = \frac{\partial S}{\partial \sigma}\delta q,$$

σ denoting the electric charge per unit area. The surface tension will be altered by a term $\partial\epsilon/\partial A$. Now

$$\frac{\partial\epsilon}{\partial A} = \frac{\dfrac{\partial S}{\partial\sigma}\delta q}{\delta A} = \sigma\frac{\partial S}{\partial\sigma}.$$

The complete expression for the surface tension thus becomes

$$\gamma = S - \sigma\frac{\partial S}{\partial\sigma} - \frac{1}{2}C\Pi^2,$$

or

$$\gamma = S - \sigma\frac{\partial S}{\partial\sigma} - \frac{1}{2C}\sigma^2 \quad \text{.....(60).}$$

Whichever side of the electric double layer is positive, its effect is opposite to that of the natural surface energy, and the term $\sigma\partial S/\partial\sigma$ is always negative, but there is no reason to suppose that its numerical value will be the same when it represents the effect of anions and cations on the electrolyte side of the double layer. The total electrocapillary curve therefore consists of parts of two parabolas which meet at the point for which $\sigma = 0$ and $\gamma = S$. Only the ascending branch has a maximum which is in general near, but not at, the point of intersection. Since the concentration of the ionic layer is always small, the variation of available surface energy can be formulated, and van Laar, by determining the constants of his detailed equations, finds that they represent the experimental results of S. W. J. Smith with great accuracy. On this confirmation of

[1] *Kon. Akad. Wetens. Amsterdam*, March, 1902, p. 560.

his theory, van Laar concludes that the capillary electrometer does not give a trustworthy means of measuring single potential differences.

In the work on electrocapillary phenomena to which we have referred, S. W. J. Smith[1] finds indications that, on changing the potential difference by external means, a leakage current will flow owing to the tendency of the electrode to revert to its original condition, so that the condenser analogy cannot be complete. He finds that a very high resistance in the potentiometer circuit changes the indications of the electrometer.

As we said on p. 281, on almost any view of the phenomena there can be no difference of potential between dilute equimolecular solutions of potassium chloride and iodide, since they are equally ionized and contain ions of equal mobilities. The electromotive force of the cell

mercury / potassium chloride / potassium iodide / mercury

ought therefore to agree with the sum of the two potential differences,

mercury / potassium chloride + potassium iodide / mercury,

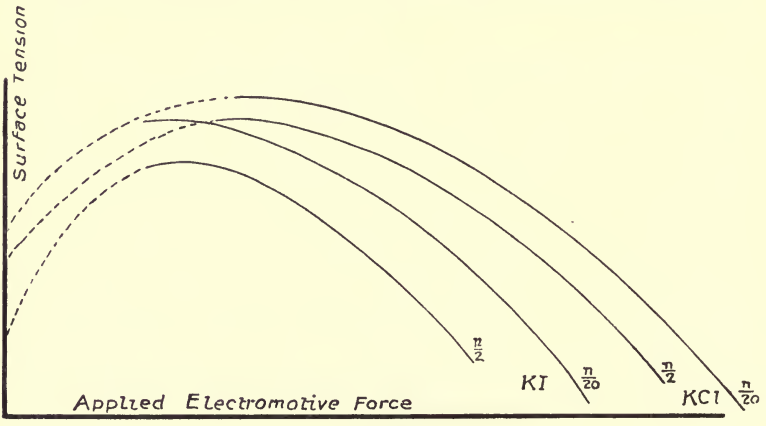


Fig. 61.

as determined by the capillary electrometer. If the latter values are estimated from the maxima of surface-tension, their

[1] *Phil. Trans.* CXCIII. A, 47 (1900).

sum for semi-normal solutions is 0·162 volt, while the cell gives 0·394 volt. Similar discrepancies occur in other cases. For these two solutions, Smith gives curves like those of Fig. 61, in which abscissae represent applied electromotive forces, and ordinates arbitrary scale readings of the electrometer. While, in their ascending portions, the two curves have different slopes, they become parallel when they descend. It is probable that the effects of the ionic polarization are then the same for both. Let E be the external electromotive force required to give the same surface tension to the capillary surface of the potassium chloride solution as E' gives to the iodide solution. Then on the parallel parts of the curves, $E - E'$ is very nearly constant. Let Π and Π' be the natural potential differences between mercury and the chloride and iodide solutions respectively. On the first hypothesis of the ordinary electrometer theory (the condenser analogy), the potential differences between the solution and the capillary meniscus for two points of equal surface tension, one on each curve, are $E - \Pi$ and $E' - \Pi'$ respectively. On the second assumption, that the sole change is an electrostatic one, and the potential differences are the same in the two cases because the surface tensions are the same, we have

$$E - \Pi = E' - \Pi',$$

or

$$\Pi - \Pi' = E - E' = a,$$

where a is an observable quantity, measured by the horizontal distance between the parallel portions of the curves. If there is no potential difference between the two solutions when in contact, the electromotive force of the cell

mercury / potassium chloride / potassium iodide / mercury

is also $\Pi - \Pi'$, and should thus be equal to a. The first four results in the following table give a comparison between the electromotive forces of such cells and the values calculated (1) by the method just described, (2) by estimating the maxima of the curves.

Solutions	Observed E.M.F. of mercury cell	Calculated E.M.F.	
		1	2
$\frac{1}{2}$ normal KCl and KI	·3940	·399	·162
$\frac{1}{10}$ „ „ „	·3503	·350	·122
$\frac{1}{20}$ „ „ „	·3381	·337	·162
1 „ KCl and KCNS	·1670	·169	—
1 „ KCl and Na_2S	·9588	·938	·581
$\frac{1}{2}$ „ „ „	·9578	·944	·581

Here again we have results which suggest that the electrostatic theory is insufficient. The maximum of surface-tension seems to depend on the nature of the anion, and, if that maximum be taken as a means of determining the natural potential difference, the electromotive force of a cell with two electrolytes having different ions apparently cannot be calculated from the two single potential differences at its electrodes. The last two lines of the table indicate the same relations in solutions where both anion and cation are different, the greater discrepancies being explained by the uncertainty regarding the contact potentials of the two solutions. Electrocapillary curves for equivalent solutions of potassium, sodium and hydrogen chlorides, which contain the same anion, coincide within the limits of experimental error throughout both the ascending and descending portions. Hence it is concluded that the effect of the anion is considerable as long as the reverse applied electromotive force is less than the natural potential difference; but the nature of the cation seems to have no appreciable influence on the potential difference throughout the whole range covered by the experiments. Assuming that the Nernst theory gives the true potential difference between two solutions, Smith, however, remarks that, although the slope of the lower portion of the descending curve varies little with the concentration of the solution, the absolute value of the surface tension for a given potential difference does show such variation. Thus the tension does not depend on the electrostatic effect alone even when the influence of the anion has presumably disappeared; there

is also a cation effect, which becomes evident as the solution grows increasingly positive with regard to the electrode, and the cation therefore tends to enter the mercury and form an amalgam. On the other hand, the anion effect increases as the electrode becomes more positive, and thus tends to dissolve.

Warburg's theory of these phenomena can be extended to the capillary electrometer on the same lines as to the case of dropping electrodes[1]. When an external electromotive force is applied, Warburg traces the increase of surface-tension to the action of the polarizing current. This current removes from the neighbourhood of the meniscus the trace of mercury salt which always dissolves from the metal into solutions containing dissolved oxygen. The salt is slowly replaced by diffusion, and the actual change in concentration is the resultant of the two opposite effects. Owing to the minute quantity of salt in the capillary tube and the slowness of the compensating diffusion, the exhaustion may be very complete. The concentration cell which is formed may thus have a considerable electromotive force. The surface-tension will reach a maximum when the whole of the mercury ions are removed from the solution near the meniscus. In order to explain the descending branches of the surface-tension curves on Warburg's theory, it has been suggested that, as the electromotive force rises, an amalgam is formed with a surface-tension naturally lower than that of mercury.

On Nernst's conception of electrolytic solution pressure, electrocapillary phenomena will be interpreted as follows. The low pressure of mercury causes positive ions to enter it even from a dilute solution. The mercury thus acquires a positive charge. An external electromotive force applied to an electrometer from solution to metal causes a temporary current, which carries more mercury ions across the interface. In the capillary tube this process at once dilutes the solution, and therefore, in accordance with the logarithmic formulae of Chapter X., makes the mercury more anodic to the electrolyte and eventually stops the current. If the concentration of the mercury ions in the solution falls to the value corresponding to the solution pressure

[1] *Wied. Ann.* XXXVIII. 321 (1889); XLI. 1 (1890).

of the metal, the potential difference disappears; if it falls below that value, the potential difference is reversed, the mercury becomes negative to the solution, and draws cations to the electrolyte side of the double layer.

On the theories of both Warburg and Nernst, when the external electromotive force is removed, the processes of diffusion should gradually reduce the differences of concentration and the displacement of the meniscus of the electrometer. Burch has found, however, that a new and good electrometer will show the same deflection of the meniscus for many hours when charged to a small fraction of a volt and then left on open circuit with its electrodes insulated from each other. Such observations indicate that for small electromotive forces, the instrument acts as a condenser of good insulation. Nevertheless, it seems certain that the changes of concentration contemplated by Warburg and Nernst must occur in some cases. It is possible that it is to the influence of such effects that are due some of the discrepancies which appear in the results of experiments on the potential differences at the surfaces of contact of mercury with electrolytes.

Electric endosmose.

Another set of electrocapillary phenomena, like those we have been considering, probably depend on the natural potential differences at the surface of separation of two unlike substances—in this case an electrolyte and an insulator. If an electric current be passed through a vessel divided into two compartments by means of a porous partition and filled with some solution, we shall find that, in general, besides the changes in concentration at the electrodes which were described on p. 207 under the head of migration, there is a bodily transfer of the liquid, usually in the direction of the current, through the porous plate. To this phenomenon the name of electric endosmose is given. It has been experimentally studied by Wiedemann[1] and Quincke[2].

If the pressure be kept constant on both sides of the partition, the volume of liquid which flows through, as measured

[1] *Elektricität*, II. 166.

[2] *Pogg. Ann.* CXIII. 513 (1861).

by the overflow, is proportional to the total electric transfer, and is independent of the area and thickness of the plate; it varies much with the nature of the solution, being greater with liquids of high specific resistance, and, in solutions of different concentrations of any one substance, is approximately proportional to the specific resistance.

If the liquid is not allowed to overflow, the pressure on one side of the porous wall will increase. The final pressure is directly proportional to the electromotive force between the faces of the partition, and therefore to the current through it; for a given current it varies inversely as the area of face of the porous wall and directly as its thickness. In this case, the flux of liquid due to the electric forces must be equal and in the opposite direction to that caused by the difference of hydrostatic pressure. Considering the porous wall to consist of a collection of capillary tubes, we can apply Poiseuille's laws to the reverse flux under the hydrostatic forces, and this explanation has been supported by Quincke, who proved that the pressure produced by electric endosmose through a capillary glass tube was inversely proportional to the fourth power of the diameter of the tube. The pressures were considerable with distilled water, but ceased to be perceptible with liquids of high conductivity such as solutions of salts and acids.

A detailed theory of the subject has been given by von Helmholtz[1], on Quincke's hypothesis of a constant potential difference between the liquid and the walls of the capillary tubes. The electric charge which resides on the outermost layer of liquid and forms the inner face of the electric double layer, will be acted on by the external electromotive force and the skin of liquid will therefore be dragged through the tube. If a difference of pressure is allowed to develop, one current of liquid is drawn forwards along the walls, and an opposite one flows down the centre of each tube under the action of the hydrostatic forces. The final pressure is reached when these two currents of liquid convey equal volumes per second in opposite directions. From these ideas von Helmholtz deduced the observed facts of electric endosmose, and calculated that

[1] *Wied. Ann.* VII. 337 (1879).

the contact potential differences involved were of the order of one volt. A modification of the theory has been given by Lamb[1], allowing for a slight slip between the liquid and the walls of the tube.

In a similar manner is explained the motion through liquids of fine particles of clay or other material under the influence of an external electromotive force, a phenomenon which has been studied by Quincke and others[2].

It has been suggested by W. N. Shaw[3] that electric endosmose constitutes an essential part of the mechanism of electrolysis, the motion of the liquid being due to the drift of complex ions made up of an ion of the salt attached to a large number of solvent molecules. The inverse proportionality between the concentration of a solution and the endosmotic effect, shows that, in very dilute solutions, such complex ions must contain many hundred or thousand water molecules; and it seems more likely that, in accordance with the usual view, electric endosmose is an independent phenomenon, not directly connected with the electrolytic process.

t is possible that the results of experiments with capillary electrometers may be influenced by electric endosmose as soon as any current flows and a potential gradient established along the capillary tube. From Quincke's observations above described, however, it seems probable that the measurements would not appreciably be affected.

Single potential differences continued.

It is evident from what has been said in the sections preceding the last, that there is some doubt whether the experiments on dropping electrodes and on capillary electrometers really enable the natural potential difference, which is involved in the electromotive force of a galvanic cell containing a mercury-electrolyte surface, to be calculated even approximately. Nevertheless, since many useful determinations of other single potential

[1] *B. A. Report*, 1887, 495.

[2] Wiedemann's *Elektricität*, II. 181.

[3] *B. A. Report*, 1890, 202.

differences, which, at all events, are relatively exact, rest on such measurements, in the present condition of the subject we must provisionally accept the value of about + 0·92 volt as the potential difference between mercury and dilute sulphuric acid, the mercury being positive to the acid. The step of potential as thus measured is in the opposite direction to that which occurs at the surface of a zinc plate. Results are obtained for other metal-electrolyte surfaces by subtracting this number, or another similarly estimated for mercury in contact with some other electrolyte, from the total electromotive force of galvanic cells arranged in the manner

metal / electrolyte / mercury.

Such indirect determinations will contain as a constant error any deviation of the primary measurement from the true value, but, as relative numbers, serving to compare the metals among themselves, they will retain their importance.

In making such experiments, it is usual to employ what is known as a normal electrode, consisting of a quantity of pure mercury covered by a layer of mercurous chloride and a solution of potassium chloride of normal concentration, that is, a solution containing one gram-equivalent per litre. An indiarubber tube ending in a glass tube leads from the solution and is filled with it (Fig. 62). Contact can thus be made between the potassium

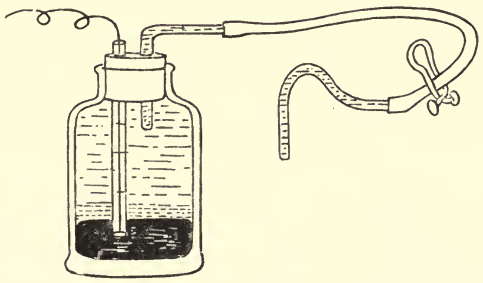


Fig. 62.

chloride and any other liquid. This electrode as measured by Lippmann's method gives a potential difference of 0·56 volt, the mercury tending to come out of solution and be deposited

as metal. The chlorides can of course be replaced by other substances when their potential with respect to mercury is known. Thus a soluble sulphate, with mercurous sulphate as depolarizer, has been used. Assuming that we may neglect the small effects at the junction of the metals, and at the surfaces of contact of unlike solutions, if such surfaces are present, the measured electromotive force of the combination metal / electrolyte / normal electrode enables the potential difference at the surface metal / electrolyte to be calculated by subtraction.

In this manner, Neumann measured the single potential differences for many metals in contact with either normal or saturated solutions of their salts. The following are some of the most important results[1].

Metal	Sulphate	Chloride	Nitrate	Acetate
Zinc	−0·524	−0·503	−0·473	−0·522
Cadmium	−0·162	−0·174	−0·122	—
Thallium	−0·114	−0·151	−0·112	—
Iron	−0·093	−0·087	—	—
Lead	—	+0·095	+0·115	+0·079
Hydrogen	+0·238	+0·249	—	+0·150
Copper	+0·515	—	+0·615	+0·580
Silver	+0·974	—	+1·055	+0·991
Mercury	+0·980	—	+1·028	—

In this table positive signs have been assigned to those metals which show a positive potential relatively to the liquids surrounding them. Assuming the accuracy of these results as absolute numbers, it follows that such metals tend to come out of solution, and the natural potential difference at their surfaces helps to drive a current in the direction to effect the deposition. Spontaneous separation of these metals, or solution of negative metals, however, will only occur if means are available for the simultaneous addition of opposite ions, or the removal of an equivalent quantity of similar ions. The numbers show that the electromotive forces of the cells used depend on the nature of the acid ion present, but Neumann also prepared centinormal solutions of many different thallium salts, and found sensibly equal values. In these solutions the ionization may be taken

[1] *Zeits. phys. Chem.* XIV. 229 (1894).

as complete, but it remains to be seen whether or not under such conditions the equality would extend to salts of all metals. There is some evidence to suggest that the variations of electromotive force with the acid ion are to be traced to the presence of mercury, cells in which two other metals are used being usually free from such discrepancies[1].

The table on the last page gives a fair idea of the single potential differences calculated from the fundamental experiments on mercury, and, for slightly oxidizable metals such as silver, it will be seen that the method leads to numbers which have an opposite sign and an even larger numerical value than those obtained for very oxidizable substances such as zinc. The intimate connexion which exists between the electromotive force of a cell and the calorimetric heats of the resultant chemical actions, when allowance is made for the usually small reversible heat effects, has already been considered on p. 236. It seems reasonable to apply the same relations to each individual part of the circuit, and we should expect that metals which are only acted on with difficulty and have small heats of oxidation, would show a very much smaller potential difference than very oxidizable metals with large heats, though probably a difference of the same sign; in fact the potential diagrams of the cell represented by the second parts of Figs. 58 and 59 seem *à priori* more likely to correspond to reality than those shown in the first parts. Moreover, in correlating these phenomena with those of the Volta contact effect between metals in air, it is probable that there will at all events be a general agreement between them. It is unlikely that metals would show a difference of sign in their potential differences with air, if that difference is due to actual oxidation or to an affinity which tends to oxidation. On the other hand, Nernst's theory of electrolytic solution pressure offers a possible explanation of the difference in sign as usually accepted. Whatever be the final outcome of the problem, we may take Neumann's numbers and similar results as true relative values, though a constant error may eventually have to be added to or subtracted from them.

[1] Paschen, *Wied. Ann.* XLIII. 590 (1891); Taylor, *Journ. Phys. Chem.* I. 1 and 81 (1896).

Electrolytic solution pressure.

Neumann's results enable the numerical value of Nernst's electrolytic solution pressure to be calculated. In the last chapter it was shown that, on the analogy of the junctions between two liquids, the potential difference between a metal and a solution might be expressed in the form $\frac{RT}{qy}\log\frac{P_m}{P}$, R being the gas constant for the gram-molecule of the metal, P_m the solution pressure of the metal, P the osmotic pressure of its ions in the electrolyte, q the charge on the monovalent gram-equivalent, and y the valency of the ions. The potential difference can be observed, and the osmotic pressure is approximately known from the concentration of the solution. Thus the electrolytic solution pressure can be calculated; the following are some of Neumann's values in atmospheres recalculated by Le Blanc.

Zinc	$9{\cdot}9\times10^{18}$	Hydrogen	$9{\cdot}9\times10^{-4}$
Iron	$1{\cdot}2\times10^{4}$	Mercury	$1{\cdot}1\times10^{-16}$
Lead	$1{\cdot}1\times10^{-3}$	Silver	$2{\cdot}3\times10^{-17}$

In the logarithmic expression, P_m denotes the osmotic pressure of the solution at which it would show no potential difference with the metal. Nernst extends this idea, and identifies P_m with a characteristic property of the metal itself, which, on the analogy of the vapour pressure of a liquid, is taken to measure the tendency of the metal to diffuse in the form of electrolytic ions in the liquid surrounding it. The legitimacy of this extension is still a matter of discussion, and, as indicated on p. 257, by writing the formula as

$$RT\log P_m/qy - RT\log P/qy, \text{ or } M - RT\log P/qy,$$

we may treat the part of the expression referring to the metal simply as a function of its properties of unknown form. Accepting provisionally, however, the solution pressure hypothesis, the absolute values given above are still open to objection, not only as based on the mercury-electrolyte difference of potential, but in another way. The formula from which they are calculated is transferred from that deduced on the assumption of the ideal gaseous laws for the junction between two liquids, and the extension of these laws to the very high pressures here dealt with is clearly unjustified.

In the derivation of the theory for liquid junctions on p. 246, it is shown that the electromotive force is measured by the integral $\int v dP$. Lehfeldt has calculated the value of this integral on the assumption that the deviation from the gaseous laws in solutions is represented by an expression of the form of van der Waals' equation for gases. Putting

$$P = \frac{iRT}{v - b}$$

we have, since in concentrated solutions i is nearly unity,

$$Eqy = \int_{P}^{P_m} v dP = RT \log \frac{P_m}{P} + b\,(P_m - P).$$

Applying this to the case of zinc in normal zinc chloride solution, we may put 22 atmospheres for P, and 0·5 volt for E; b is assumed to be the volume of a gram-molecule of the salt in the solid state, about 46 cubic centimetres. The value of the solution pressure P_m can then be calculated, and comes out about 2×10^4 atmospheres, instead of about 10^{19}, as deduced from the simple logarithmic formula. It is clear that such considerations as these enable the deviations of concentrated solutions from the ideal gaseous laws to be estimated, and Lehfeldt has calculated the osmotic pressures of such solutions from measurements of the electromotive forces of concentration cells.

We shall reconsider the hypothesis of solution pressure under the head of electrolytic diffusion.

Electrochemical series.

It was one of the objects of the early experimenters to arrange the metals in order in an electrochemical series. The two tables of potential differences, set forth on pp. 268, 296, are quantitative solutions of this problem under given conditions. Whereas it was formerly thought that the metals occupied the same relative positions in all circumstances, it is now obvious that the potential differences which they yield will depend on the nature of the surrounding medium, and, if that medium is a solution, on the concentration of the dissolved substance, though if a table of electrolytic solution pressures could be calculated, it would enable the effects of concentration to be eliminated.

The general accuracy of the theories explained above indicates that a metal immersed in the solution of one of its salts should be the less electropositive as the concentration of its ions in the solution increases. If the metal dissolves as a compound salt, as do gold and silver in cyanide solutions, it may be that the metal can exist in the solution in the form of simple ions in very small quantity only[1].

In accordance with this result, the electromotive force of such metals as gold and silver in solutions of cyanides is very high, and places them in a position in the electrochemical series different from that which they occupy when the metals are studied in contact with solutions of their own salts or the corresponding acids. As stated in the last chapter, Hittorf found that in the cell $Cu / KCN / K_2SO_4 / ZnSO_4 / Zn$, copper is dissolved when a current flows.

The contact potentials of different metals with cyanide solutions have also been studied by von Oettingen[2] and by Christy[3]. The latter observer traces the influence of the concentration of a solution of potassium cyanide on its potential difference against gold, and shows that the rate at which gold dissolves when shaken with the liquid is a function of this potential difference and also of the amount of dissolved oxygen. As a combination of these two effects, the rate of solution of the gold reaches a maximum at a concentration of ten to twenty per cent. of potassium cyanide, and then again decreases as that proportion is exceeded.

Polarization.

Another aspect of the subject now under consideration is given by an examination of the phenomena of polarization. As we said in Chapter VIII., it requires a certain minimum electromotive force to drive a permanent current through an electrolyte between electrodes which are not dissolved. If a single Daniell's cell be connected through a galvanometer with two platinum plates immersed

[1] See footnote p. 255.

[2] *Journ. Chem. and Metallurgical Soc. South Africa*, 1899.

[3] *Amer. Inst. Mining Engineers, Trans.* xxx. (1899), reprinted as *Bulletin of Depart. Mining, etc., Univ. of California.*

in dilute sulphuric acid, the galvanometer is at first deflected. The current, however, rapidly falls off, and soon sinks nearly to zero. If the platinum plates are now disconnected from the cell, and joined with each other through the galvanometer, they will send a current through it in the reverse direction. The plates are said to be polarized. The electromotive force of polarization, in the case we have chosen, soon diminishes, so that in order to measure its maximum value, the connexions must be rapidly reversed. Raoult[1] found that a speed of reversal of one hundred alternations a second was enough to secure this result. The best method of experimenting is to use a tuning-fork commutator which vibrates very rapidly.

If the electromotive force is gradually raised from a very small value, the reverse force of polarization is also found to rise, keeping equal to that applied, until a nearly constant limit is reached. A further rise in the applied electromotive force causes little or no more increase in the polarization, and the current through the solution can then be calculated from Ohm's law by taking as the effective electromotive force the value found by subtracting that of polarization from the force externally applied.

Decomposition voltage.

The phenomena of polarization have been very fully studied by Le Blanc[2]. There is a certain decomposition value for the applied electromotive force, beyond which a permanent current flows. Le Blanc found that the decomposition voltage can be easily and exactly determined for salts from which a metal is precipitated, the current starting from that point to rise proportionally to the electromotive force; but for other salts, as well as for acids and alkalies, the measurements are more uncertain.

The following decomposition values were found with platinum electrodes for salts from which the metal is precipitated; the salts were mostly in normal solutions.

[1] *Ann. Chim. Phys.* IV. 2. 326 (1864).

[2] *Zeits. phys. Chem.* VIII. 299 (1891); or Le Blanc's *Elektrochemie*, Eng. Trans. p. 247.

SALTS.

Zinc sulphate	2·35 volts	Cadmium nitrate	1·98 volts
Zinc bromide	1·80 „	Cadmium sulphate	2·03 „
Nickel sulphate	2·09 „	Cadmium chloride	1·88 „
Nickel chloride	1·85 „	Cobalt sulphate	1·92 „
Lead nitrate	1·52 „	Cobalt chloride	1·78 „
Silver nitrate	0·70 „		

Whereas the values given in the above table for metallic salts vary from metal to metal, the values for acids and alkalies show a maximum decomposition point, which is approached by most of these compounds and exceeded by none.

ACIDS.

Sulphuric	1·67 volts	Pyrotartaric	1·57 volts
Nitric	1·69 „	Trichloracetic	1·51 „
Phosphoric	1·70 „	Hydrochloric	1·31 „
Monochloracetic	1·72 „	Hydrazoic	1·29 „
Dichloracetic	1·66 „	Oxalic	0·95 „
Malonic	1·69 „	Hydrobromic	0·94 „
Perchloric	1·65 „	Hydriodic	0·52 „
Dextrotartaric	1·62 „		

BASES.

Sodium hydrate	1·69 volts	Diethylamine ($\frac{1}{2}$ normal)	1·68 volts
Potassium hydrate	1·67 „	Tetramethyl ammonium hydrate ($\frac{1}{8}$ normal)	1·74 „
Ammonium hydrate	1·74 „		
Methylamine ($\frac{1}{4}$ normal)	1·75 „		

Acids and alkalies which evolve hydrogen and oxygen on electrolysis, show the maximum decomposition voltage nearly independently of the concentration of the solution. For acids which are more easily decomposed, the numbers increase on dilution with a simultaneous change in the nature of the products.

The use of other non-oxidizable electrodes such as gold or carbon instead of platinum, leads to different numerical results, though the relations between them remain unaltered. The differences may be explained by remembering that, although the resultant chemical process is in each case the liberation of

hydrogen and oxygen, the production of bubbles of gas at the surface of a metal, which does not occlude the gas, is an essentially irreversible operation depending on conditions which may well vary from metal to metal[1].

Polarization at each electrode.

The electromotive force of polarization evidently consists of two parts, one depending on the electrical work done at the anode, and the other on that at the cathode. In order to examine these separately, an arrangement due to Fuchs was used by Le Blanc[2]. The tuning-fork commutator is adapted to a double U-tube apparatus shown in Fig. 63. The primary

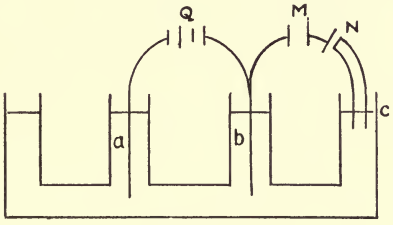


Fig. 63.

or polarizing current is passed from Q between the electrodes a and b. If the electrode b is to be examined, the bent glass tube of the normal electrode described on p. 295 is inserted at c, and the effect of the cell so formed is balanced by an adjustable electromotive force at M, an electrometer being used as indicator. The potential difference between the plate b and the liquid can then be found by subtracting that of the normal electrode and that at the contact of the two solutions at c. As the primary current from Q is increased from zero, it is found that the electromotive force of polarization is at first nearly equal to that of the primary current, but it gradually comes to

[1] In this connexion reference may be made to a paper by Nernst and Dolezalek [*Zeits. Elektrochem.* May 10, 1900]; and another, containing a criticism on it, by C. J. Reed [*Journ. Phys. Chem.* v. 1 (1901)], on the "Gas Polarization of Lead Accumulators."

[2] *Zeits. phys. Chem.* XII. 333 (1893); XIII. 163 (1894); also *Electrochemistry*, p. 244.

a nearly constant value, though Le Blanc states that no exact final limit is ever reached.

When the solutions which deposit metals are examined in this way, Le Blanc finds that at the decomposition point the polarization potential difference at the cathode is equal to the potential difference which a plate of the metal itself gives if placed in contact with the solution, both, of course, depending on the value taken for the fundamental mercury-electrolyte difference of potential. The polarization at a junction is thus exactly correlated with the single potential difference, which can be measured by experiments on capillary electrometers or dropping electrodes. If, as previously explained, we refer the total potential difference to a combination of molecular and ionic effects, Le Blanc's results indicate that electrolytic polarization is an ionic phenomenon—a natural result to anticipate. As the external electromotive force is gradually increased from zero, the measured potential difference at the cathode, like the total electromotive force of polarization, rises also, approaching a limit, though the electromotive force necessary to reach this limit is often less than that required to give the maximum polarization of the whole apparatus which includes the anode also. The limit seems to be reached when the deposit of metal on the electrode is enough to cover its surface with a continuous layer. The converse phenomenon has been studied by Oberbeck[1], who deposited small quantities of the metal of a salt solution on a platinum plate, and then measured the potential difference between the plate and a solution of the same salt placed in contact with it. As the amount of deposit was increased, this potential difference rose, and finally reached the value found for a solid plate of the metal. As a final result of all these investigations, it is concluded that the deposition and solution of metals from solutions of their salts are reversible processes. The single potential differences exhibited in Neumann's table on p. 296, may therefore also be taken as measuring the polarization when the metal is electrolytically deposited from its solution in the salts there indicated.

[1] *Wied. Ann.* xxxi. 336 (1887).

Evolution of gases.

In considering the total effects of polarization the anode also has to be taken into account. When the anode is of platinum or a similar metal, gas is usually evolved there, and it thus becomes of great importance to determine how far the conditions of reversibility hold good in the evolution of gas at an electrode. As we have seen, a minimum electromotive force is required to continually electrolyse a dilute solution of sulphuric acid in water; when gold or bright platinum electrodes are used, about 1·7 volts are necessary. The reverse electromotive force of polarization is, however, only 1·07 volts, and as is well known, if the hydrogen and oxygen are collected in tubes and kept in contact with platinum electrodes, an arrangement called Grove's gas battery is obtained, which furnishes a secondary electromotive force of 1·07 volts, and will yield a current as long as any gas remains. Thus the development of gas at a bright platinum surface is an irreversible process. When, however, the electrodes are coated with platinum black by previously passing a current backwards and forwards between them through a solution of platinum chloride, Le Blanc proved that the decomposition point was 1·07 volts; so that, with platinized electrodes, the process is reversible. The difference is explicable when we remember that platinum occludes a large amount of gas. The platinized electrodes absorb the gases when slowly developed, and when the plates become saturated, if parts of them are outside the liquid, they can gradually give up the gases by diffusion without the formation of bubbles. Thus, if an external electromotive force of 1·07 volts be applied, the system is in equilibrium, while, if the applied electromotive force exceeds or falls short of that value by an infinitesimal amount, an indefinitely small current will flow one way or the other, and the gases are slowly set free or dissolved. The arrangement is therefore reversible, and the thermodynamic treatment of the effects of pressure, etc., on the electromotive force of the oxy-hydrogen gas battery, which was given on p. 240, applies equally to their effects on the reverse electromotive force of polarization in the decomposition of water between platinized

electrodes. We may therefore in this case also write the equation then deduced,

$$E = \frac{RT}{qy} \log \frac{p_1}{p_2},$$

where R is the usual gas constant for one gram-molecule, T the absolute temperature, q the charge of electricity passing when one univalent gram-ion is liberated, y the valency of the ions, and p_1 and p_2 the pressures in the two cases considered.

Now if p_2 be gradually reduced, the value of this expression can be made as great as we please, and thus, at a certain very low pressure, the reverse electromotive force must vanish, and below this pressure actually be reversed, so that water would decompose spontaneously. This critical pressure will be so low that it is quite out of reach of experimental confirmation; in fact the vapour pressure of the water itself would prevent its ever being reached.

The information that the decomposition of water could theoretically be effected at a low pressure by a very small electromotive force is exceedingly striking, for the heat developed by the direct chemical combination of oxygen and hydrogen at constant pressure is nearly independent of the absolute value of that pressure. It furnishes a good illustration of the want of proportionality between the heat of chemical union and the electromotive force when other transformations of energy are involved, and shows the need of the second term in von Helmholtz's equation, p. 236,

$$E = \lambda + \theta \frac{dE}{d\theta}.$$

Let us now return to the case when gold or bright platinum electrodes are used instead of platinized ones. As we have said, the decomposition point is then 1·7 volts, while the reverse electromotive force is still only 1·07 volts, showing that the process is irreversible. Bright electrodes have very little power of absorbing gas; consequently if an electromotive force between 1·07 and 1·7 volts be applied, the gases cannot be removed from the electrodes nearly fast enough by diffusion, and, when the solution in the neighbourhood of the electrodes becomes saturated with dissolved gas, the evolution will cease.

Slow diffusion from the liquid into the air and back through the liquid will however go on, and this process allows more gas to be evolved, while a slight leakage current continually flows, as indicated by the galvanometer. In order to produce a permanent large current and a constant evolution of gas in appreciable quantities, it is necessary to raise the electromotive force till it is able to cause the formation of bubbles at the surface of the electrodes, a process which involves an amount of work depending on the surface-tension, the state of the electrodes and other uncertain and irreversible conditions. That these conditions vary with different kinds of electrode is shown by the unequal potential differences needed to liberate hydrogen at cathodes of platinum, gold, lead, copper, etc. In such cases, when bubbles of gas are formed, part of the available energy of the chemical action is not expended on electrical separation; thus the reverse electromotive force, which depends on the free energy of this separation, is less, and the process is not reversible.

Electrolytic separations.

It will be noticed that the 1·7 volts needed to evolve oxygen and hydrogen at bright platinum electrodes is the maximum value of the decomposition point of solutions of acids and alkalies (p. 302). This fact is explicable if we consider in detail the process of electrolysis in such cases. All the ions in the solution, of whatever nature, are acted on by the electric forces, and must therefore all carry the current by moving through the solution; as, indeed, was shown by the experiments of Hittorf. At the electrode, however, if more than one kind of ion is present, that kind will first be deposited which has the lowest deposition value. Now we shall find later that in water, even when pure, a certain number of hydrogen and hydroxyl ions are always present, and unless they are removed in some way, these ions will cause hydrogen and oxygen to be evolved before any substances in the solution which possess higher deposition voltages can appear at the electrodes.

Now for acids and alkalies, the electrolytic processes allow this preferential action to occur. The hydrogen ions derived

from the electrolyte in one case, and its hydroxyl ions in the other, travel to the electrode at which they can respectively be converted into neutral hydrogen and oxygen. Thus while in the interior of the solution the current is almost entirely carried by the ions of the acid or the base, the transmission from the solution to the electrode is effected primarily by the ions of the water. From solutions of some salts also, hydrogen and oxygen are evolved; but here the conditions are different. Alkali is developed at the cathode, and its hydroxyl ions, combining with some of the hydrogen ions of the water, enormously reduce the number available. Thus the potential difference required to liberate the hydrogen at the electrode is increased, in accordance with a relation to be afterwards deduced and already used on p. 253 to explain the high electromotive forces of certain concentration cells.

Returning to the consideration of acids and alkalies, we see that the decomposition voltage of such of them as contain ions of higher values than hydrogen and hydroxyl cannot rise above the potential difference which liberates hydrogen and oxygen. Those acids on the other hand, which, like hydrochloric, contain an anion of low deposition point, show a smaller decomposition value when present in fairly concentrated solutions. As the concentration falls, it becomes difficult for the diffusion of the acid in solution to replace fast enough the chlorine ions which are removed from the layer of liquid in contact with the electrode. Increasing numbers of hydroxyl ions are therefore used to convey the current into the electrode, and this causes a rise in the polarization, which in dilute solutions reaches the maximum 1·7 volts. From strong solutions of hydrochloric acid the gases evolved are hydrogen and chlorine, but as dilution proceeds, the chlorine is gradually replaced by oxygen from the hydroxyl. This rise in the polarization is well seen in the following table, due to Le Blanc.

2	normal	hydrochloric	acid,	decomposition	point	1·26 volts
$\frac{1}{2}$	„	„	„	„	„	1·34 „
$\frac{1}{6}$	„	„	„	„	„	1·41 „
$\frac{1}{16}$	„	„	„	„	„	1·62 „
$\frac{1}{32}$	„	„	„	„	„	1·69 „

The products of the continuous electrolysis of any mixed solution, containing two metals, depend on conditions more complicated than those which control the initial decomposition voltage of the solution or the polarization at one electrode. It is evident that the conditions determining the appearance of a second kind of ion of higher deposition point depend on such things as the current density, the transport numbers for the different ions present, the rate of diffusion of the dissolved substances, the existence and intensity of convection currents in the liquid and any mechanical mixing or stirring. The initial decomposition voltage of a solution, however, does not involve these dynamical problems, and solely depends on the potential differences required for the liberation of the ions first appearing at the two electrodes. If we accept the logarithmic expression for the electrolytic solution pressure, it is easy to see that two ions can only be simultaneously liberated by an electromotive force E when, with the usual notation,

$$\frac{RT}{qy_1}\log\frac{P_{m_1}}{P_1}=\frac{RT}{qy_2}\log\frac{P_{m_2}}{P_2},$$

or, for two monovalent ions, when

$$\frac{P_1}{P_2}=\frac{P_{m_1}}{P_{m_2}},$$

that is, when the partial osmotic pressures of the two ions in the liquid are in the same ratio as their solution pressures[1]. Even if this result be only a rough indication of the conditions of the problem, it serves to show that enormous differences in concentration would be necessary in order that the two metals of different deposition-voltages should be deposited together from a well-stirred solution, by a current of small intensity.

Experiments confirming these conclusions have been made by Sand on mixed solutions of copper sulphate and sulphuric acid, in which convection was prevented. He finds that copper, which, at a copper electrode, has a deposition value lower than that of hydrogen by about 0·507 volt, is first liberated at the

[1] Nernst, *Zeits. phys. Chem.* XXII. 541 (1897); Sand, *Proc. Phys. Soc. Lond.* XVII. 496 (1901).

cathode. As the current is increased, hydrogen also appears; but this is due to the exhaustion of copper from the layers of solution in contact with the electrode which proceeds more rapidly than the replacement effected by the diffusion of the salt. By efficient stirring it is possible to prevent any evolution of gas in cases where, without stirring, over sixty per cent. of the electro-chemical equivalents liberated would be hydrogen.

Electrolysis has long been used to separate metals from each other. The theory of this process will now be clear. Let us suppose that we have a mixed solution of zinc and copper sulphates. The deposition point of copper is $-0{\cdot}515$ volt, and that of zinc $+0{\cdot}524$ volt. Thus if the total electromotive force applied be enough to give a potential difference at the cathode greater than $-0{\cdot}515$ volt but less than $+0{\cdot}524$ volt, copper only will be deposited, for although its deposition point rises as the amount of copper gets less, this change is very small, and all traces of copper which could be detected by chemical analysis will be removed from the solution before the deposition point rises to that of zinc. If the electromotive force at the cathode be now increased above $+0{\cdot}524$ volt, the zinc likewise can be separately removed from solution.

Even without this adjustment of electromotive force, if the solution be kept well stirred to prevent the local exhaustion of one metal at the electrodes, complete separation can be nearly effected. For, as we have seen, as long as there is any of the metal of lower deposition point present, none of the other is liberated. This principle is used in a process of copper refining. A plate of pure copper forms the cathode in a bath of copper sulphate. The anode is a thick plate of impure copper, probably containing metals both less and more easily deposited than copper. The bath is stirred, and when the current flows, copper and all more oxydizable metals are dissolved, while the less oxydizable metals, such as gold and silver, fall to the bottom of the vessel, for while copper is present in excess the current will dissolve it rather than more resisting metals. In the neighbourhood of the cathode, however, there will be a large excess of copper together with other metals, such as zinc, more

easily oxydizable and therefore of higher deposition points. As long as any copper is near, therefore, none of the other metals are deposited, and pure copper is obtained at the cathode.

On the other hand, by increasing the current density, it is usually possible to exhaust the one metal from the layers of solution next the electrode faster than either stirring or diffusion will replace it. The other metal must then also be used by the current, and, by proper adjustment of conditions, it is possible to deposit alloys, the percentage composition of which can be altered by varying the current density.

CHAPTER XII.

THE THEORY OF ELECTROLYTIC DISSOCIATION.

Introduction. Osmotic pressure of electrolytes. Additive properties of electrolytic solutions. Dissociation and chemical activity. The mass law. Equilibrium between electrolytes. Thermal properties of electrolytes. Heat of ionization. Dissociation of water. The function of the solvent. Hydrolysis. Conclusion.

Introduction.

THROUGHOUT our investigation of the electrical properties of solutions we have constantly been led to infer that the ions of electrolytes are to a certain extent independent of each other. The flow of the current is in accordance with Ohm's law, and as we have already pointed out, that law implies freedom of interchange between the parts of the dissolved molecules. The existence of specific coefficients of mobility as characteristic properties of certain ions in very dilute solutions, involves the idea of independent migration, and suggests that the freedom of the ions from each other persists during the greater part of the time, and is not merely a power of interchange at the moments of molecular collision. If it were only a momentary freedom, the convective passage of the ions in opposite directions through the liquid, indicated by Faraday's law, would be explained by a continual handing on of the ions from molecule to molecule. The ions would work their way along by taking advantage of the intermolecular collisions, and the ionic velocities would depend on the frequency of these collisions; a frequency, which, as indicated by the kinetic theory, depends on the square of the concentration. Now, as we saw on page 213, the conductivity

of a solution varies as the product of the concentration and the relative ionic velocity; on this view, then, the conductivity will be proportional to the cube of the concentration. The facts described on page 203 do not bear out this result. In dilute solutions, the conductivity is proportional to the concentration, and, as the concentration rises, the conductivity increases at a slower rate. It is difficult to see how these relations could hold except as a consequence of an almost complete migratory freedom of the ions of dilute solutions, and very strong evidence is thus obtained in favour of a theory of ionic dissociation.

Preconceived ideas would not, perhaps, lead us to expect that substances, which, like the mineral salts and acids, show great chemical stability when solid, should almost completely be dissociated into their ions when dissolved in water. It must, however, be remembered that it is precisely these bodies which possess the greatest chemical activity, that is to say, most readily exchange their parts with those of other substances. That a solution of hydrochloric acid, for example, does not exhibit the properties of dissolved hydrogen and chlorine, though it has been urged as an objection, is not a valid argument against the theory of dissociation, for the ions are certainly in conditions differing from those in which the atoms of the same elements exist in their usual state. Whether or not there is combination between the ions and the solvent, and whatever be the exact relation between the ions and the charges they carry, we are at least certain that a definite quantity of electricity has to pass between an ion and the electrode before the substance can be liberated in a normal chemical state, say as gaseous hydrogen or chlorine. The energy associated with a substance when ionized must therefore be very different in quantity and character from that associated with it when in its normal chemical condition, and there is no reason to assume identity of properties in the two states.

It has been suggested that, if really dissociated from each other, the two ions of a dissolved salt would generally diffuse at different rates, and ought therefore to be separable. If such separation occurred, however, electrostatic forces between the ions would at once arise and increase till further division was

prevented. Nevertheless, some separation should undoubtedly occur, and, as a matter of fact, a volume of water in contact with the solution of an electrolyte is found to take, relatively to the solution, a potential of the same sign as the charge on the ion which has the greater mobility and therefore the quicker rate of diffusion. The phenomena involved will be studied in Chapter XIII.

An experiment described by Ostwald[1] is instructive in connexion with this subject. A membrane of copper ferrocyanide can be prepared which will allow potassium chloride in solution to pass through it, but is quite impermeable to barium chloride. Now, according to the theory, the chlorine ions of this salt will again pass, since they could do so in the first case, but the electric forces will prevent any considerable separation from taking place. If, however, we place some substance like copper nitrate on the other side of the membrane, the chlorine ions, which diffuse in one direction, are replaced by nitric acid ions, which diffuse in the other. In this way electrostatic charge is prevented, and the process will continue till we soon find nitrate mixed with the barium chloride, and chloride mixed with the copper nitrate. The salts cannot have directly reacted, for neither alone can pass through the membrane, but the exchange is readily intelligible on the hypothesis that the ions possess migratory independence.

The dissociation required by the theory is a separation of the ions from each other, securing complete migratory independence. There is nothing to suggest that the ions are free from all chemical combination. As pointed out in the chapter on theories of solution, the hypothesis of electrolytic dissociation is entirely independent of any particular view as to the nature of solution or the physical mode of action of the osmotic pressure. All that is required to interpret the electrical phenomena is the freedom of the migrating ions from each other; they may quite possibly be combined in some way with the solvent. If we take a chemical view of the nature of solution, it is in fact necessary, as shown on page 174, to imagine such combinations between

[1] *B. A. Report*, 1890, p. 332.

the ions and the solvent in order to explain the abnormal osmotic pressures of electrolytes. We may perhaps represent what occurs by supposing that double molecules, such as $NaCl.2H_2O$, are formed, and dissociated into $\overset{+}{Na}.H_2O$, and $\overset{-}{Cl}.H_2O$, complex ions analogous to those described on pages 226—229, for the existence of which there is definite evidence.

On the other hand it may even be that a double decomposition goes on, as suggested by Reychler[1], a molecule of sodium chloride, for example, decomposing with water thus:

$$\overset{+}{Na}\,\overset{-}{Cl} + HOH = \overset{+}{Na}\,OH + \overset{-}{HCl}.$$

The water here is separated into parts which are non-electrical; a positive molecule of the composition $\overset{+}{NaOH}$, and a negative molecule $\overset{-}{HCl}$ are consequently formed. These molecules are not the same as ordinary soda and hydrochloric acid, which themselves are imagined to react with water in accordance with the equations

$$\overset{+}{Na}\,\overset{-}{OH} + HOH = \overset{+}{Na}\,OH + \overset{-}{HOH}$$

and

$$\overset{+}{H}\,\overset{-}{Cl} + HOH = \overset{+}{H}OH + \overset{-}{HCl}.$$

The acid, by the interchange of its hydrogen, becomes negatively electrified, and produces a positive molecule of water which acts as the cation; the alkali itself becomes a positive ion, and produces a negative molecule of water to form the anion. This hypothesis may not accurately represent the facts —the suggested decomposition of water under the action of dissolved electrolytes into non-electrical hydrogen and hydroxyl cannot readily be accepted—but it does not seem to be contradicted by any of the electrical relations; and it is from the consideration of this and other similar ideas that we may hope to ascertain the essential features of the dissociation theory.

[1] *Outlines of Physical Chemistry*, Eng. trans., London and New York, 1899, p. 216.

Osmotic pressure of electrolytes.

In solutions of electrolytes the osmotic pressure and the correlated effects, the depression of the freezing-point and the lowering of the vapour pressure, are abnormally great. When an organic body such as cane sugar is dissolved in water, the osmotic pressure effects of dilute solutions are found, approximately at any rate, to agree with the values deduced by Van 't Hoff's theory. The osmotic pressure of dilute dissolved gases can be deduced by the principles of energetics either from the observed solubility relations, or from general molecular theory, and the reasonable extension of the results to solutions of other substances is justified by experimental measurements in many different solvents, examples of which, due to Raoult, are given on pages 156 and 157. Such theoretical and experimental considerations prove that, when water is used as solvent, the lower series of values, obtained with organic solutes, are normal; it is the higher values characteristic of electrolytic solutions, which need further explanation.

As long as a solution is dilute enough for the particles of solute to be outside each other's sphere of action, theory indicates that the osmotic pressure of a number of dissolved molecules has a value identical with that of the pressure the same number of gaseous molecules would exert at the same temperature when confined in a volume equal to that of the solution. Thus the osmotic pressure effects of dilute substances must depend on the number and not on the nature of the dissolved molecules. When experiments yield abnormally small values, it follows that the number of the solute molecules is less than that indicated by the chemical formula weight; it is then natural to conclude that aggregation of molecules to form complexes has occurred. When, on the other hand, abnormally great values are obtained for solutions of electrolytes, it is necessary to infer that the number of solute particles is increased, and that some of their molecules have dissociated. Attempts have been made to explain the phenomena by an association of solvent molecules instead of a dissociation of those of the solute, but the general theory indicates that it is the volume and not the state of molecular

aggregation of the solvent that is involved; moreover, in the particular case of vapour pressure which led to the idea of the association of the solvent, the equations of page 128 clearly show that such an association would not affect the osmotic pressure.

As soon as Van 't Hoff[1] made known his investigations on osmotic pressure they were applied to the theory of electrolytic dissociation by Planck[2] and by Arrhenius[3]. Planck showed that the abnormally great osmotic pressure effects of electrolytes, when considered from the point of view of thermodynamic theory, required the hypothesis of some form of electrolytic dissociation. Arrhenius pointed out that the amount of dissociation thus existing in a solution might be estimated by two independent methods; it might be determined by the comparison of the actual equivalent conductivity with its value at infinite dilution, or by the measurement of the osmotic pressure effects, of which the importance had been recognized by Van' t Hoff.

The depression of the freezing-point has been more thoroughly investigated than the other correlated properties, and as the experimental error is probably less, a comparison may rightly be instituted between the results of this method and the electrical ones. Following Arrhenius, let us suppose that every electrolytically active molecule produces an abnormally great osmotic pressure, and that its effect is proportional to the number of ions into which it can be resolved. Thus the effect of an active molecule of potassium chloride should be twice that of an inactive one, and the effect of a molecule of potassium sulphate, which in dilute solutions yields two K ions and one SO_4 ion, should be three times that of an undissociated molecule.

If then, in a certain solution, we have m inactive and n active molecules, each of the latter giving k ions, the total

[1] *Kongl. Svenska Akad. Handl.* XXI. 38 (1885); *Zeits. phys. Chem.* I. 481 (1887).

[2] *Wied. Ann.* XXXII. 499 (1887).

[3] *Zeits. phys. Chem.* I. 631 (1887); Eng. trans. Harper's *Science Series*, IV. 47.

osmotic pressure produced will be proportional to $m + kn$, whereas the normal osmotic pressure would be proportional to $m + n$. By measuring the conductivity we can, for the dilute solutions of simple salts (see p. 225), find the fraction of the number of molecules which is at any moment active. Let us call it α. Then, on Arrhenius' theory

$$\alpha = \frac{n}{m+n},$$

so that, if the ratio of the actual osmotic pressure to the normal is called i,

$$i = \frac{m+kn}{m+n} = 1 + (k-1)\,\alpha \ldots\ldots\ldots\ldots\ldots\ldots (61).$$

This same ratio can also be found by direct experiment on the depression of the freezing-point, for by Van 't Hoff's equation we know the normal value, and if t be the observed depression for a solution of one gram-equivalent per litre,

$$i = \frac{t}{1{\cdot}86}.$$

We can thus compare the value of i as directly determined by observations on the freezing-point, with its value as calculated from the conductivity. The table on the opposite page is part of that given by Arrhenius[1] for aqueous solutions.

It will now be seen that there are two relations involved in the dissociation theory. Firstly, the number of ions into which a molecule must be resolved in order to explain its electrical behaviour when completely dissociated in a very dilute solution should be the same as the number required to give its observed osmotic pressure; secondly, in dilute solutions of simple salts, where the phenomena are not obscured by complex ions or changing ionic viscosity, as the concentration rises, the abnormally great osmotic pressure should diminish with the coefficient of electric ionization. Since the publication of Arrhenius' original paper, the results of which were accepted as a rough proof of the approximate accuracy of both these relations, a great quantity of experimental work has been undertaken; some of it must now be passed in review.

[1] *Zeits. phys. Chem.* II. 491 (1887).

Substance dissolved	No. of gram-equivalents per litre	*i* observed from freezing-points	*i* calculated from conductivities	*α* coefficient of ionization
A. *Non-Conductors.*				
Methyl alcohol CH_3OH	0·1	0·90		
	0·485	0·96		
	0·97	1·00		
Ethyl alcohol C_2H_5OH	0·125	0·97		
	0·62	1·01		
	1·24	1·05		
Phenol $C_6H_5.OH$	0·101	0·96	1·00	0
	0·216	0·96		
	0·558	0·93		
Cane Sugar $C_{12}H_{22}O_{11}$	0·0445	1·08		
	0·0947	1·11		
	0·316	1·12		
	0·809	1·34		
	1·01	1·43		
B. *Electrolytes.*				
Lithium hydrate LiOH	0·127	1·98	1·90	·90
	0·317	1·89	1·86	·86
Acetic acid CH_3COOH	0·135	1·05	1·01	·01
	0·337	1·04	1·01	·01
	0·842	1·01	1·00	·00
Phosphoric acid H_3PO_4	0·077	1·38	1·32	·11
	0·146	1·27	1·25	·08
	0·319	1·22	1·20	·07
Sodium chloride NaCl	0·0467	2·00	1·88	·88
	0·117	1·93	1·84	·84
	0·194	1·87	1·82	·82
	0·539	1·85	1·74	·74
Silver nitrate $AgNO_3$	0·056	2·02	1·86	·86
	0·140	1·90	1·81	·81
	0·341	1·77	1·73	·73
Potassium sulphate K_2SO_4	0·0364	2·68	2·45	·72
	0·091	2·35	2·33	·66
	0·227	2·21	2·18	·59
	0·455	2·04	2·06	·53
Calcium chloride $CaCl_2$	0·0476	2·74	2·52	·76
	0·119	2·62	2·42	·71
	0·199	2·66	2·34	·67
	0·331	2·73	2·24	·62
Copper sulphate	0·0393	1·33	1·41	·41
	0·112	1·15	1·34	·34
	0·254	1·03	1·27	·27
	0·523	0·94	1·22	·22
	0·973	0·92	1·18	·18

To investigate the first relation it is necessary to measure the electrical conductivity and the freezing-point of solutions

so dilute that the ionization may be taken as complete, or, at all events, that its value at infinite dilution may be estimated. The freezing-point experiments are complicated by sources of error pointed out in Chapter VI. In Raoult's book[1] on "Cryoscopie" are given the results obtained by Loomis at a concentration of 0·01 gram-molecule of salt to 1000 grams of water, *i.e.* 0·01 normal, as in themselves trustworthy and in accordance with the best of other results known at the time. The following are the molecular depressions of the freezing-point for certain substances in aqueous solution, the concentration being expressed as gram-molecules of solute per thousand grams of water.

Potassium hydrate	3·71	Nitric acid	3·73
Hydrochloric acid	3·61	Potassium nitrate	3·46
Potassium chloride	3·60	Sodium nitrate	3·55
Sodium chloride	3·67	Ammonium nitrate	3·58
Sulphuric acid	4·49	Calcium chloride	5·04
Sodium sulphate	5·09	Magnesium chloride	5·08
Magnesium sulphate	2·66	Zinc sulphate	2·90

In the first group are substances which are shown by the electrical properties to yield in solution two monovalent ions. On the dissociation theory, therefore, the osmotic pressure effects should, at high dilutions, have double their normal value. The normal value for the molecular depression of the freezing-point is 1·857, as calculated from the osmotic pressure theory, and confirmed by experiments on dilute aqueous solutions of non-electrolytes (see page 147). Twice this value is 3·714, a number to which all the observed molecular depressions of substances in group 1 closely approximate. The electrical behaviour of bodies in the second group similarly indicates dissociation into three ions, producing a theoretical molecular depression of 5·57. The experimental numbers differ from this value by perhaps 10 per cent., but the error is in the right direction since the electrical conductivities at the concentration

[1] Paris, Oct. 1901.

used by Loomis in these freezing-point experiments, namely, about 0·01 normal, show that the ionization is still far from complete in the salts containing divalent ions. The corresponding error is still greater in the salts of the third group, which yield two ions, both divalent; the molecular depression should be again 3·714, greater by about a third than the observed values. All discrepancies are thus of the kind to be expected from a consideration of the electrical phenomena; and the first group, the salts of which are about 95 per cent. ionized at the concentration used in the cryoscopic experiments, yield very concordant results.

In the investigation of the freezing-points of very dilute solutions carried out by E. H. Griffiths, to which reference was made on pages 147 and 158, results for salts with divalent ions have not yet been published. The molecular depression of potassium chloride at a concentration of about 0·0003 normal was found to be 3·720, exactly double, within the limits of experimental error, the number given by an equivalent solution of cane sugar. At this concentration the conductivity indicates that 99·7 per cent. of the salt is dissociated.

Thus the evidence at present available goes to support the accuracy of the first relation of Arrhenius' theory in the case of aqueous solutions. The observed depressions never appreciably exceed the theoretical values, and the discrepancies in the other direction are readily explicable by incomplete ionization. In fact consideration shows that the relation can only be exact for those solutions which reach a definite limit of equivalent conductivity as the dilution is increased; it is only these solutions that are fully ionized.

Passing to solutions in solvents other than water, we find that sufficient data are not available to decide whether the same relation between the electrical and the osmotic phenomena holds good. The difficulties of experiment are much increased, and no observations on osmotic pressure effects seem to have been made on solutions in which the dilution was carried far enough to secure a constant value for the equivalent conductivity and so justify the assumption of complete ionization. In many aqueous solutions, such as those of acetic acid

and ammonia in particular, complete ionization cannot be experimentally reached; and, without definite evidence, we cannot assume that it is ever obtained in another solvent. Measurements on stronger solutions are of little use, for as soon as the dissolved particles come within each other's sphere of influence their change of available energy by dilution will not be independent of the nature of the solvent, and the thermodynamic deduction of the gas-value for the osmotic pressure ceases to be valid. Moreover, for non-aqueous solutions, we have little knowledge of such electrical constants as the transport numbers, and it is not safe to conclude that the ions are of the same nature as in water. In alcoholic solutions, at any rate, what little evidence is forthcoming indicates that complex ions are very numerous, even at moderate dilutions, (see pages 195 and 218), and any such complexity must diminish the number of dissolved particles, and consequently the osmotic pressure effects. Kahlenberg, however, states that solutions of diphenylamine in methyl cyanide show abnormally low molecular weights, and yet are not conductors of electricity[1]. Such a result perhaps indicates a dissociation yielding products which are not electrically charged, or a non-electrical double decomposition with the solvent. Until further observations have been made it is impossible to say whether or not the first relation suggested by the dissociation theory holds for non-aqueous solutions.

The second relation enunciated by Arrhenius indicates that the coefficient of ionization measured electrically should agree with its value calculated from the osmotic pressure effects; but this relation can only hold within very narrow limits of concentration. The thermodynamic theory of osmotic pressure is valid only when the solute particles are beyond each other's sphere of influence, and any further addition of solvent can consequently not affect that part of their available energy which is due to their connexion with the solvent. For greater concentrations, the osmotic pressure will depend on the nature of the solvent and of the solute, and on the interaction between them. Again, if complex ions are present, and, in any case, as

[1] *Jour. Phys. Chem.* v. 344 (1901); vi. 48 (1902).

soon as the concentration becomes great enough to affect the ionic fluidity, the ratio of the actual to the limiting equivalent conductivity, as shown on p. 225, ceases to measure the fraction of the number of molecules which are resolved into independent ions. Moreover, except in solutions of such simple salts as potassium chloride, etc., there is some doubt whether the limiting value of the equivalent conductivity has ever been reached, and if not, even in dilute solution, the electrical measurements do not give the true coefficient of ionization. Nevertheless, experiments on these lines are of great interest; confirmation of the relation for dilute aqueous solutions of simple salts would be valuable evidence that the Arrhenius relation gives, in such cases, a complete explanation of the phenomena, and the amount of divergence in other cases would supply useful indications of the nature and amount of the disturbing influences. It must be clearly recognized that, while the dissociation theory requires the agreement in the numbers of the ions indicated by the electrical and osmotic methods in the few cases in which the conductivity phenomena show the ionization to be complete, it is far from suggesting that the first relation holds in other cases, or that the second relation exists except for a limited range of concentration of salts which in dilute solution are fully ionized. As soon as the concentration begins to increase, the complications we have indicated are appreciable, and the relation between the electrical and the osmotic values of the ionization coefficient must become more and more inexact. Stress is laid on these restrictions because the relations under consideration have played a great part in the history of the dissociation theory, and the want of quantitative agreement in the results of the two lines of research has often been adduced to deny the claims of the theory to give a true explanation of the difference between electrolytic and non-electrolytic solutions.

It may here be pointed out that relations, which are true when the system possesses the properties of dilute matter, must be expected to begin to fail at much smaller concentrations in the case of electrolytes than of non-electrolytes. On the supposition that the forces between atoms and molecules

are electrical, the force between two electrically bipolar molecules will quickly diminish as the distance between them increases—probably as the fourth power. The force thus rapidly becomes insensible beyond a certain small range, the sphere of molecular action; but the force between two dissociated ions is of a different order. Here we have positive and negative charges which are not permanently connected to opposite charges to form molecular doublets. The forces will be more of the nature of those between small isolated electrified bodies, and their variation with distance will approximate to the law of inverse squares; their range is greatly increased, and ionic influence will not rapidly vanish beyond a definite limit in the same way as do the intermolecular forces. We might expect, for example, that, for cane sugar, the molecular depression of the freezing point should keep constant throughout a much greater variation of concentration than for the solution of a metallic salt, even when the latter is corrected for ionization. It is possible that, as the concentration increases, the electric forces between the dissociated ions become sensible before any re-combination can occur; if so, the ionic velocities, and therefore the conductivity, would be reduced before the ionization ceases to be complete, and the coefficient α of p. 224 would not represent the ionization even at great dilution. On the other hand, the osmotic pressure effects might be affected also at about the same concentration, though not necessarily to the same extent, and perhaps any such inter-ionic electric forces as are here contemplated may, for the purposes of the properties we are considering, be truly reckoned as combination. At all events, the forces would interfere with that complete migratory independence of the opposite ions as regards each other which may be taken as the meaning of complete ionization.

References to cryoscopic determinations on solutions of electrolytes have been made in the chapter on freezing points, pp. 153 to 158. Many of the results have been compared with the ionizations as measured by Kohlrausch at 18° or Ostwald at 25°; but to obtain a satisfactory basis of comparison, the electrical data also must be determined at the freezing point.

Experiments at 0°, on solutions of moderate dilution, have been made by R. W. Wood[1], Archibald[2], and Barnes[3], the limiting values of the equivalent conductivity being estimated by reference to Kohlrausch's data. Other experiments were made by Kahlenberg and Hall[4] and by the present writer[5], who carried the dilution far enough to reach the limiting equivalent conductivity of simple salts. The experiments were planned in connexion with those of Griffiths on freezing points, and were made in a platinum cell similar to his apparatus. The results showed an appreciable difference when the ionizations were determined at 0° and at 18°. The following values were obtained from smoothed curves drawn between the cube root of the concentration and the equivalent conductivity, and represent the most probable numbers for the ratio μ/μ_∞ of the actual to the limiting equivalent conductivity throughout the range of concentration employed. The values for magnesium sulphate were obtained later from experiments in a glass cell.

It will be seen that definite limits were found for the equivalent conductivities in the cases of potassium chloride and permanganate and of barium chloride. In these solutions, therefore, complete ionization was reached at the concentrations indicated. In the cases of the other salts used, potassium bichromate and ferricyanide and copper sulphate, no exact limit was found, and the value of the equivalent conductivity corresponding to complete ionization had to be estimated by exterpolating the curves. For sulphuric acid which, as at 18°, reaches a maximum equivalent conductivity at a certain dilution, and then falls off again as the concentration is still further diminished, the maximum was taken as the limit, a mode of procedure which, however, almost certainly leads to too high values for the ionization coefficients.

[1] *Zeits. phys. Chem.* XVIII. 3 (1895); *Phil. Mag.* [5] XLI. 117 (1896).
[2] *Trans. Nov. Sco. Inst. Sci.* X. 33 (1898).
[3] *Ibid.* X. 139 (1899); *Trans. Roy. Soc. Canada*, II. 6 (1900).
[4] *Jour. Phys. Chem.* V. 339 (1901).
[5] *Phil. Trans.* A. CXCIV. 321 (1900); *Zeits. phys. Chem.* XXXIII. 344 (1900).

Equivalent conductivities at 0°, *referred to the limiting values as unity.*

n = number of gram-equivalents of solute per thousand grams of solution.

n	$n^{\frac{1}{2}}$	KCl	$KMnO_4$	$\frac{1}{2}BaCl_2$	$\frac{1}{2}H_2SO_4$	$\frac{1}{2}CuSO_4$	$\frac{1}{2}MgSO_4$	$\frac{1}{3}K_3FeCy_6$	$\frac{1}{2}K_2Cr_2O_7$
0·00001	0·0215	1·000	1·000	1·000	..	0·998	0·983	0·998	0·991
0·00002	0·0272	1·000	1·000	1·000	..	0·993	0·976	0·996	0·980
0·00005	0·0368	1·000	1·000	0·998	0·876	0·981	0·963	0·991	0·952
0·0001	0·0464	0·999	1·000	0·995	0·942	0·967	0·950	0·985	0·929
0·0002	0·0585	0·998	0·999	0·990	0·983	0·947	0·932	0·977	0·902
0·0005	0·0794	0·996	0·998	0·980	1·000	0·908	0·899	0·961	0·880
0·001	0·1000	0·992	0·993	0·969	0·993	0·863	0·864	0·944	0·870
0·002	0·1260	0·987	0·986	0·953	0·971	0·807	0·814	0·919	0·864
0·005	0·1710	0·976	0·971	0·925	0·928	0·717	0·720	0·876	0·863
0·01	0·2154	0·962	0·955	0·896	0·880	0·638	0·659	0·834	0·858
0·015	0·2466	0·952	0·944	0·876	0·848	0·591	0·618		0·853
0·02	0·2714	0·944	0·934	0·864	0·822	0·557	0·587	..	0·847
0·03	0·3107	0·932			—		0·545		

The investigation has lately been extended in glass apparatus to greater concentrations, and the following smoothed values have been obtained :—

n	$n^{\frac{1}{3}}$	KCl		$\frac{1}{2}BaCl_2$	$\frac{1}{2}CuSO_4$	$\frac{1}{2}MgSO_4$
·03	·311	·932	·929	·843	·512	·545
·05	·368	·917	·913	·813	·468	·493
·10	·464	·896	·888	·778	·405	·433
·20	·585	·874	·861	·742	·348	·373
·40	·737	·858	·833	·710	·294	·315
·50	·794	·855	·823	·699	·275	·295
1·0	1·000	·856	·794	·665	·230	·213
1·2	1·063	·860	·786	·657	·218	·188
1·5	1·145			·645	·208	·149
2·0	1·260			·632	·194	·090

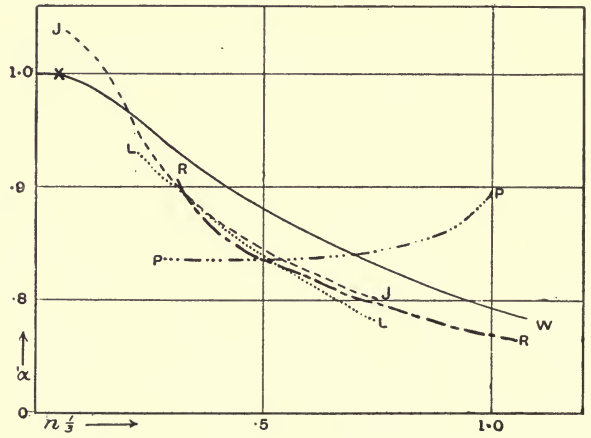
The first column under KCl, like those under all the other salts, gives the value of μ / μ_∞ when the concentration is expressed in terms of gram-equivalents of salt per thousand grams of solution. In the second column under KCl, the concentration is expressed per thousand grams of solvent. This method, if applied to the other salts would, in a similar way, reduce the calculated results.

The corresponding freezing point experiments are not yet completed, and an exact comparison of the two lines of research is not possible. If, however, we accept Griffiths' result for potassium chloride as establishing the first relation, namely, the agreement between the numbers of the ions at infinite dilution as estimated in the two ways, we can take $1{\cdot}858\,k$, where k is the number of the ions, as the limiting value of the molecular depression, and calculate the ionization α from cryoscopic determinations on stronger solutions. The following comparisons with the electrical measurements described above may be given, n being expressed in gram-molecules of salt per thousand grams of solvent.

Potassium chloride. KCl = 74·59.

n	$\delta T/n$	α (Raoult)	μ/μ_∞
·0291	3·542	·906	·929
·0585	3·466	·864	·908
·1173	3·416	·837	·883
·2368	3·376	·816	·854
·4813	3·328	·790	·825
1·000	3·286	·767	·794
	α (Jones recalculated)	α (Loomis)	
·005	·992	—	·976
·01	·932	·937	·962
·02	·919	·911	·942
·05	—	·881	·913
·1003	·855	·849	·888
·2012	·835	·821	·860
·4048	·803	·783	·832

In the annexed diagram, the smooth curve W denotes the electrical values of μ/μ_∞, and the dotted lines indicate the



ionizations as deduced from the cryoscopic observations of Raoult (R), Loomis (L), Jones (J), and Ponsot (P). The cross

shows the concentration at which Griffiths found complete ionization. Accepting his result, it follows that Jones' numbers, at great dilution at any rate, are too high, while the complete difference of Ponsot's curve from those of other observers makes it unsafe to lay stress on his experiments. We are thus left with the results of Raoult and Loomis, and the lower part of Jones' curve as a basis of comparison with the electrical measurements. As a general conclusion, we may perhaps say that there are indications that the electrical and cryoscopic curves approach each other at greater dilutions, and perhaps also at greater concentrations. Throughout the range at which a direct comparison can be made, however, there is a considerable difference between the two sets of results. This difference is greater than has been usually supposed. The electrical curve, deduced from conductivity measurements made at 18°, which has generally been adopted as the basis of comparison, lies below the curve for 0° given in the diagram, and happens nearly to coincide with the cryoscopic results. The question cannot be regarded as settled, but the evidence at present available indicates that the ionizations as measured in the two ways become consistent only at extreme dilution, even in simple salts such as potassium chloride.

The divergencies between the cryoscopic results of different observers, considerable in the case of potassium chloride, become even more conspicuous for more complicated salts, and in the present position of the subject no useful purpose would be served by a detailed examination. It seems that, in some cases at any rate, the curves cross each other at moderate concentration, the electrical becoming lower than the freezing point results. In barium chloride solutions, the change occurs within the range of comparison given by Loomis' experiments; it is possible that some of the agreements that have been obtained may depend on accidental conjunctions of this nature, and would fail at lower and higher concentrations.

More accurate determinations of the freezing points are needed before such comparisons as these can be taken as a satisfactory basis for theoretical generalizations. Collections of

Barium chloride.

Loomis			
$n=2M$	$\delta T/M$	α	μ/μ_∞
·02	4·99	·843	·865
·04	4·95	·832	·831
·10	4·761	·781	·778
·20	4·676	·759	·742
·40	4·627	·745	·710

the present data have been made by MacGregor[1] and Kahlenberg[2].

Passing as before to solutions in solvents other than water, we again find the difficulties of experiment much increased. Many observations have been made, but very seldom has the dilution been pushed to such extremes as are necessary to produce complete ionization in aqueous solutions. The phenomena seem to be more complicated, and sometimes the equivalent conductivity increases with concentration even in fairly dilute solutions[3]. Limiting values of the equivalent conductivity for salts of the alkali metals dissolved in methyl and ethyl alcohol have however been obtained by increasing the dilution by Fitzpatrick[4], Völlmer[5], and Zelinsky and Krapiwin[6].

For solutions in these solvents, then, it is possible to calculate the dissociations at moderate dilutions by determining the ratio of the equivalent conductivities. To compare these results with the osmotic values, it is necessary to use the vapour pressure or the boiling point method, as the freezing points of these solvents are very low. A collection

[1] *Trans. Nova Scotia Inst. Sci.* x. 211 (1899—1900); *Phil. Mag.* [5] L. 505 (1900).

[2] *Journ. Phys. Chem.* v. 339 (1901).

[3] Kahlenberg, *Journ. Phys. Chem.* v. 342 (1901).

[4] *B. A. Report*, 1886, p. 328; *Phil. Mag.* XXIV. 378 (1887).

[5] *Wied. Ann.* LII. 328 (1894).

[6] *Zeits. phys. Chem.* XXI. 35 (1896).

of results of such comparisons has been made by A. T. Lincoln[1], who gives the following tables from boiling point experiments by Woelfer, and conductivity experiments by Völlmer.

Salt	Concentration in per cents.	Ionization	
		From boiling point	From conductivity
Solutions in methyl alcohol.			
Lithium chloride	0·45	0·63	0·57
Potassium iodide	0·36	0·61	0·79
Sodium iodide	0·44	0·87	0·74
Potassium acetate	0·48	0·48	0·63
Sodium acetate	0·40	0·49	0·63
Solutions in ethyl alcohol.			
Lithium chloride	0·9	0·35	0·32
Potassium acetate	1·07	0·18	0·27
Potassium iodide	0·78	0·29	0·49
Silver nitrate	0·53	0·65	0·38
Sodium iodide	2·14	0·27	0·45
,, ,,	0·68	0·51	0·56
Sodium acetate	0·97	0·01	0·24

In alcoholic solutions, what little evidence is available indicates that complex ions are very frequent even at moderate dilutions (see pp. 195 and 218), and the above results show that, as we should expect, the disturbing factors have greater influence than in aqueous solutions. The results for sodium iodide suggest that better agreement would be obtained at smaller concentrations.

Experiments, summarized in Lincoln's paper, on acetone by Carrara, Laszozynski, and Dutoit and Aston, and on pyridine by Laszozynski and Gorski, indicate limiting values for the equivalent conductivities of the iodides of the alkali metals when dissolved in these solvents[2]. Lincoln's measurements on

[1] *Journ. Phys. Chem.* III. 457 (1899).

[2] Carrara, *Gazz. Chim. Ital.* XXVII. 1. 207 (1897); Laszozynski, *Zeit. Elektrochem.* II. 55 (1895); Dutoit and Aston, *Compt. rend.* CXXV. 240 (1897); Laszozynski and Gorski, *Zeit. Elektrochem.* IV. 290 (1897).

silver nitrate in pyridine show no sign of reaching a limit, but his greatest dilution was only 784 litres per gram-molecule[1]. Many other solvents give conducting solutions, but, in them, limiting values of the equivalent conductivity have seldom or never been obtained. A general account of the work that has been done on non-aqueous solutions will be found in Lincoln's paper. Cases in which the boiling or freezing points of conducting solutions indicate molecular weights equal to or greater than the normal have been pointed out by Kahlenberg[2]. Such phenomena probably indicate association of the non-ionized solute molecules.

Additive properties of electrolytic solutions.

Many attempts have been made by chemists to trace connexions between the physical properties of compounds and their chemical constitution. Details can be found in any book on physical chemistry. The general result may be summarized by saying that, while some properties, such as the atomic volumes, the atomic heats, and the power of magnetic rotation of the plane of polarization of light, seem to be permanent characteristics of the elements and keep nearly the same values even when those elements change their state of combination, such additive relations are limited to a few properties, and never seem to be more than approximations.

In solutions of electrolytes, additive relations are applicable to many more properties, and are much more accurately true. The explanation of these results by means of the hypothesis of the practical independence of the constituents of the solutes

[1] A detailed study of this solution would be useful, for in it Faraday's law has been confirmed by Skinner (*B. A. Report*, 1901, p. 32); from boiling point experiments Werner concluded that the molecular weight is nearly normal (*Zeits. Anorg. Chem.* xv. 23 (1897)); while, between dilutions of one and forty litres, the transport numbers for the cation have been found by Schlundt to be: 1 litre, 0·326; 2 litres, 0·342; 10 litres, 0·390; 40 litres, 0·440 (*Jour. Phys. Chem.* vi. 168 (1902)). This rapid change indicates the existence of complex ions. Schlundt remarks that, as a rule, the experiments of Hittorf and others show that the transport number for the cation increases rapidly with dilution in solutions of salts which show a marked affinity for the solvent.

[2] *Journ. Phys. Chem.* v. 342 (1901).

was suggested by several observers, even before the development of the electrolytic dissociation theory. That theory indicates that when the ionization is complete, the difference between any physical property of a solution and the corresponding property of its solvent should be compounded additively of the differences produced by the two ions. When the ionization is not complete, the differences referred to must be similarly compounded of those produced by the undissociated molecules and the dissociated ions. It should thus be possible to express the numerical values of the various properties in terms of the state of ionization, by means of an expression of the form

$$P = P_w + K(1-\alpha)n + L\alpha n$$

where P is the numerical value of any property, such as the density, etc., P_w the value of the same property for the solvent under the same conditions, n the molecular concentration of the solution, α the ionization coefficient, and K and L two constants independent of the concentration. MacGregor has supported this equation for many properties of dilute solutions by tabulating known data[1]. An extended account of the additive relations of salt solutions will be found in Ostwald's *Lehrbuch der Chemie.* A short summary only is here attempted.

Valson[2] found that the specific gravities of salt solutions could be calculated from a table of moduli of the elements of the substance dissolved, the modulus for each element being experimentally determined. The relation is better investigated, however, by considering the specific volume instead of its reciprocal the specific gravity, and Groshaus[3] found that the molecular volume of the dissolved salt was, in dilute solution, the sum of two constants, one determined only by the acid and the other only by the base. The densities and thermal expansions of solutions have since been redetermined by Bender[4], who confirmed Valson's conclusions. The thermal expansion of

[1] *Phil. Mag.* [5] XLIII. 46 and 99 (1897).
[2] *Compt. rend.* LXXIII. p. 441 (1874).
[3] *Wied. Ann.* XX. p. 492 (1883).
[4] *Wied. Ann.* XXII. 184 (1884); XXXIX. 89 (1890).

salt solutions is more uniform the more the concentration is increased, the curved temperature-volume diagram for water becoming more straight as salt is added. Ostwald[1] has measured the volume-changes accompanying the neutralization of bases by acids, and shown that, here again, additive relations appear. The subject has been fully discussed by Nicol[2].

Similar phenomena appear when we study the colour of a salt solution[3], which is found to be produced by the superposition of the colours of the ions and the colour of the undissociated salt. If the absorption spectra of a series of coloured salt solutions containing a common ion are examined, the additive character of the colour is well seen, the absorption bands due to the common constituent being unaffected by the presence of the other part of the salt. The light transmitted through a solution is composed of all those rays which have been absorbed by neither constituent. Anhydrous cobalt chloride is blue, while in cold aqueous solution all cobalt salts are red. Red, then, is the colour of the cobalt ion, and only appears when the salt is more or less dissociated. When cobalt chloride is dissolved in alcohol, the conductivity is very low, showing very incomplete ionization. The colour is, accordingly, the blue of the undissociated salt. If we slowly add water to this solution, the ionization gradually increases, and the colour changes to purple and then red. An aqueous solution, boiled with potassium cyanide, is decolorised, for a cobalti-cyanide, $K_3Co(CN)_6$, has been formed; the ions of this compound are 3K and $Co(CN)_6$; the free cobalt ions no longer exist, and the solution ceases to respond to the usual tests for cobalt. That the red colour is really due to the ionization, and not to a hydrate formed between the cobalt salt and the solvent, is indicated by the additive nature of the phenomena; for, like many other properties, the colour of non-electrolytes depends on the constitution and is not additive. The use of indicators, which show the presence of acids or bases by a change in colour, depends upon similar phenomena. Thus para-nitrophenol is a weak

[1] *Lehrbuch*, or *Solutions*, p. 257.

[2] *Phil. Mag.* XVI. 121; XVIII. 179 (1883—4).

[3] Ostwald's *Lehrbuch; Zeits. phys. Chem.* IX. 584 (1892).

acid, very little dissociated. The addition of an alkali, soda for example, causes the corresponding salt to be formed. This is largely dissociated, and the intensely yellow colour of the ion $C_6H_4NO_2.O$ is at once seen.

A rise of temperature generally reduces the dissociation of a salt in solution, and increases the number of combined molecules —the accompanying increase of conductivity being brought about by a still greater reduction in the viscosity which the solution opposes to the motion of the ions. We should expect, therefore, on heating a coloured solution in which this temperature relation exists, that the colour would become more like that of the undissociated salt. Thus anhydrous copper chloride is a yellow solid, and the combination of this with the blue of the copper ion produces the green colour of the strong solution. On adding water the colour gets more blue, but on heating it goes back to green. Other cases have been described by J. H. Gladstone[1].

Similar additive relations have been traced in the refraction coefficients, which were found by Gladstone to be additive properties in solutions of active—*i.e.* dissociated—salts, in the optical rotatory powers, in the surface tensions, and in the viscosities of salt solutions; while Perkin, from the phenomena of magnetic rotation, concluded, without reference to the dissociation theory, that salts were dissociated into acid and base. The thermal capacities are complicated in that a change of temperature usually causes a change in the state of dissociation to an amount dependent on the nature of the substance; but, in completely dissociated solutions, the thermal capacity is also an additive property[2].

Dissociation and chemical activity.

The rapidity and ease with which reactions occur between solutions of electrolytes are in sharp contrast with the difficulty and delay usually experienced in producing chemical changes in organic substances. The close connexion between chemical activity and

[1] *Phil. Mag.*, 1857, [4], XIV. p. 423.

[2] Marignac, *Ann. Chim. et Phys.*, 1876, [5], VIII. p. 410.

electrolytic conductivity was noticed by Hittorf, and Arrhenius, who afterwards investigated the subject, was able to establish definite numerical relations.

The existence of specific coefficients of affinity, which are characteristic properties of individual acids and bases whatever the reaction in which they are engaged, is clearly recognized in modern chemistry. The relative strengths of these affinities may be measured in different ways with consistent results. If one acid acts on the sodium salt of another, some of the sodium salt is decomposed, and, unless its acid is removed from the sphere of action by evaporation or precipitation as fast as it is formed, eventually certain quantities of both sodium salts and both acids will be left in solution. The relative amounts will finally be the same whichever possible pair of components we use as reagents. The final composition of the solution cannot, in general, be ascertained by chemical means, for the addition of a new substance would alter the equilibrium. Physical methods of investigation have therefore been employed.

Thomsen determined how much of the sodium salt of one acid was decomposed by another, by measuring the heat evolved during the action. He thus measured the ratio in which the base is shared by the acids—a ratio which may be said to express their relative avidities. Ostwald[1] also investigated the relative avidities of acids for potash, soda, and ammonia, and proved them to be independent of the base. The method employed was to measure the changes in volume caused by the action. The results are given in column I. of the table which follows, the avidity of hydrochloric acid being taken as one hundred.

Another method is to allow some acid to act on an insoluble salt, and to measure the quantity of substance which goes into solution. Determinations have been made with calcium oxalate, which is easily decomposed by acids, oxalic acid and a soluble calcium salt being formed. The avidities of acids relative to that of oxalic acid are thus found, so that the acids can be compared among themselves. Their relative avidities as thus measured are given in column II. of the table.

A property of acids, at first sight unconnected with the

[1] *Lehrbuch der Allg. Chemie.*

avidity, is their accelerating influence on such actions as the "inversion" of cane sugar, which consists in its transformation into dextrose and laevulose. It has long been known that strong acids produce much greater accelerating effects than weak acids, the acid itself being in all cases unchanged. The relative strengths of acids as thus determined agree with their avidities for decomposing the salts of other acids. Another instance of accelerating action is seen in aqueous solutions of methyl acetate, which, if allowed to stand, undergo a very slow decomposition into alcohol and acid. This process is much quickened by the presence of a little dilute foreign acid, though the accelerator remains unchanged. It is again found that the influences of different acids on this action may be taken as specific coefficients of affinity. The results of this method are given in column III.

Finally in column IV. the electrical conductivities of normal solutions of the acids have been tabulated. A better basis of comparison would be the ratio of the actual to the limiting conductivity; but, since the conductivity of acids is chiefly due to the hydrogen, the limiting value is nearly the same for all, and the general result of the comparison would be unchanged.

As we have already noticed, the electrolytic conductivities of solutions of different mineral acids attain approximately equal values and their ionizations are nearly complete. Similar phenomena are observed in the case of their chemical affinities. The values of the affinity for hydrochloric, nitric and other strong acids are practically the same, and cannot by any means be increased. Ostwald has found that the introduction of oxygen, sulphur or a halogen, which increases the affinity of a weak acid (compare acetic acid with the three chloracetic acids), has no effect on the affinity of strong acids. The limit has evidently been reached, and the whole substance obtained in a state of activity. In each column of the following table the number for hydrochloric acid has therefore been made equal to 100.

Acid	I	II	III	IV
Hydrochloric	100	100	100	100
Nitric	102	110	92	99·6
Sulphuric	68	67	74	65·1
Formic	4·0	2·5	1·3	1·7
Acetic	1·2	1·0	0·3	0·4
Propionic	1·1		0·3	0·3
Monochloracetic	7·2	5·1	4·3	4·9
Dichloracetic	34	18	23·0	25·3
Trichloracetic	82	63	68·2	62·3
Malic	3·0	5·0	1·2	1·3
Tartaric	5·3	6·3	2·3	2·3
Succinic	0·1	0·2	0·5	0·6

Similar methods can be used for determining the relative strengths of bases. The avidities can be compared by sharing an acid between two bases competing for it; and their influence on the rate of saponification of methyl acetate gives the accelerating power[1]. Since the velocity of the hydroxyl ion is less than that of the hydrogen ion, the conductivities yield a less accurate method of comparison than in the case of acids, and the ionizations have therefore been calculated for the concentration of one-fortieth normal, at which the accelerating power was measured.

Base		Accelerating power	Ionization
Lithium	hydroxide	100	97
Sodium	„	98	97
Potassium	„	98	97
Ethylammonium	„	12	16
Ammonium	„	2	2·5

The difficulties and the experimental errors of some of these chemical measurements are very considerable, and, in many cases, the solutions of the acids given in the table are not of comparable concentrations. Nevertheless, the remarkable general agreement of the results is quite enough to show the intimate relation which exists between the chemical activity of

[1] J. Walker, *Physical Chemistry*, London, 1899, p. 277.

electrolytes in aqueous solution and their electrical conductivity. For solutions in other solvents no such numerical data are available. Kahlenberg has shown that chemical reactions which are practically instantaneous occur in non-electrolytic solutions in benzene[1]. As an example, dry hydrochloric acid gas passed into a solution of copper oleate in benzene produced at once a heavy brown precipitate of copper chloride, though the solution, even at the instant of reaction, showed no more conducting power than did the pure benzene. Again, an insulating solution of stannic chloride in benzene mixed with the solution of copper oleate, gave instantly a copious precipitate. It seems, then, that electrolytic ionization is not in all cases the mode of operation of rapid chemical action, and that the encounters between two molecules must sometimes be accompanied by chemical interchanges.

The mass-law.

The phenomena of reversible chemical action have already been considered from a kinetic standpoint on pp. 205 and 206. The results can also be obtained by an application of the principles of energetics. The most direct way to treat the problem is to consider the increase of available energy due to the appearance of new molecules or atoms of given species during the process of chemical change[2]. This increase in free energy will involve two terms; one expressing the work a done in forming the particle at the temperature chosen and at a standard pressure, and another giving the work required to bring by isothermal operation the new substance when formed to the actual pressure at which the system exists. If the system is a gas or dilute solution, the second term will be of the form $RT \log p/p_0$, where p is the actual and p_0 the standard pressure. Thus the change in the available energy of the system is $a + RT \log bC$, an expression already used on p. 26, where a is a function of the temperature T, R is the gas constant per gram-molecule and has the same value for all kinds of dilute matter, C is the final number of molecules of the given species per unit volume, and b is a constant expressing the dilution of the molecules at the standard

[1] *Jour. Phys. Chem.* VI. 1 (1902).

[2] Larmor, *Phil. Trans.* A. CXC. 276 (1897).

pressure and at the existing temperature. A reaction in the system involves the disappearance of molecules of some of the species present, and the appearance of others to an equivalent amount. When equilibrium is reached, the change of available energy arising from a further slight transformation of the kind considered must vanish; thus

$$n_1(a_1 + RT\log b_1C_1) + n_2(a_2 + RT\log b_2C_2) + \ldots = 0,$$

or, $$RT(\log b_1^{n_1}b_2^{n_2}\ldots + \log C_1^{n_1}C_2^{n_2}\ldots) = -(n_1a_1 + n_2a_2 + \ldots),$$

where $n_1, n_2, \ldots$ are the numbers of the molecules of the different types which are involved in the reaction, reckoned positive when they appear, negative when they disappear. We then see that

$$C_1^{n_1}C_2^{n_2}\ldots = K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(62),$$

K being a function of the temperature alone. This expression is the mass-law of chemical equilibrium, originally derived by Guldberg and Waage from statistical considerations.

This law of mass action has been applied to reversible chemical actions such as the dissociation of gaseous nitrogen peroxide and the like processes, and has been found to lead to results in accordance with the observed facts. It has been extended to electrolytic dissociation by Ostwald. For a binary electrolyte such as potassium chloride, it is natural to suppose that the change consists in the dissociation of one molecule into two ions; in this case in the equation of equilibrium n_1 will be -1, and n_2 and n_3 will each be $+1$, so that the equation becomes

$$C_1^{-1}C_2C_3 = K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(63),$$

or, since the concentration of the two ions must be the same,

$$C_1^{-1}C_2^2 = K \ldots\ldots\ldots\ldots\ldots\ldots\ldots(64),$$

where C_1 denotes the molecular, and C_2 the ionic concentration. This result is explained on kinetic principles by assuming that the rate of dissociation is proportional to the active mass C_1 of the remaining molecules; and that the rate of recombination varies as the frequency of collision between the ions, a frequency which is proportional to the product of the active masses of the ions, that is to C_2^2. For equilibrium, the two rates of transformation must be equal, and we regain the mass equation.

Considering one gram-molecule of electrolyte dissolved in a volume V of solution, the ionization being α, we have

$$\left(\frac{1-\alpha}{V}\right)^{-1}\left(\frac{\alpha}{V}\right)^2 = K,$$

or

$$\frac{\alpha^2}{V(1-\alpha)} = K \quad \text{.....(65).}$$

This equation is called Ostwald's dilution law. It should represent the effect of dilution on the ionization of binary electrolytes; and, for small concentrations, when the ionization may be measured by the ratio of the actual equivalent conductivity to its value at infinite dilution, an experimental confirmation of its accuracy should be possible. Many observations show, however, that the law fails to express the ionization of strong acids and salts, though Ostwald has confirmed it with considerable accuracy in the case of weak acids with small coefficients of ionization. For such bodies $1-\alpha$ is nearly equal to unity, and only varies slowly with dilution. The equation then becomes

$$\frac{\alpha^2}{V} = K,$$

or

$$\alpha = \sqrt{VK} \quad \text{.....(66),}$$

so that the molecular conductivity should be proportional to the square root of the dilution. If we determine α for a number of solutions of different strengths, and use our results to calculate K, we may expect the values obtained to be constant. The following table is given by Ostwald:

Acetic acid.

V	μ	μ/μ_∞	K
8	4·34	·0119	·0000180
16	6·10	·0167	179
32	8·65	·0238	182
64	12·09	·0333	179
128	16·99	·0468	179
256	23·82	·0656	180
512	32·20	·0914	180
1024	46·00	·1266	177

V is the number of litres containing one gram-molecule; μ the molecular conductivity (in mercury units), and μ_∞ its maximum value which is calculated as 364 from the velocities of the acetic acid ion and of hydrogen, determined by Kohlrausch from the conductivity of sodium acetate and mineral acids.

The following are further examples of Ostwald's experiments.

Cyanacetic acid.

V	μ	$100\,\frac{\mu}{\mu_\infty}$	K
16	78·8	21·7	0·00376
32	105·3	29·1	373
64	139·1	38·4	374
128	176·4	48·7	361
256	219·1	60·5	362
512	260·9	72·0	361
1024	297·3	82·1	368

Formic acid	K = ·0000214	Propionic acid	·0000134
Acetic „	·0000180	Butyric „	·0000149
Monochloracetic acid	·00155	Isobutyric „	·0000144
Dichloracetic „	·051	Isovaleric „	·0000161
Trichloracetic „	1·21	Caproic „	·0000145

If we have once determined the constant K for any electrolyte, we can, by the help of the equation, calculate the conductivity for any dilution. Ostwald considers that this constant, K, gives the "long sought numerical value of the chemical affinity."

If we choose states of dilution V_1 and V_2 for two different substances, such that the products V_1K_1 and V_2K_2 are equal, then $\frac{\alpha^2}{1-\alpha}$, and therefore α, must be the same for both. If we alter both dilutions in the same ratio, the products V_1K_1 and V_2K_2 are still equal, so that the dilutions at which two substances are dissociated to the same extent are always proportional, whatever the absolute values of the dilution. This was experimentally discovered by Ostwald before he had applied the theory of dissociation to electrolytes.

As already stated, the dissociation of highly ionized electrolytes does not conform to Ostwald's dilution law. The failure occurs not only in the case of acids and alkalies, when the conductivity curves are abnormal, but also in solutions of normal salts. Thus Ostwald gives the following numbers calculated from Kohlrausch's measurements for potassium chloride.

V	α	K
10	0·873	0·60
20	0·903	0·41
100	0·956	0·21
500	0·939	0·18
1000	0·994	0·16

Rudolphi[1] has given an empirical relation which seems to hold for such cases, though no physical meaning has been attached to it. The equation is

$$\frac{\alpha^2}{\sqrt{V}(1-\alpha)} = K, \quad \text{or} \quad \frac{\alpha^4}{(1-\alpha)^2 V} = K_1.$$

The values of the first constant for potassium chloride are:

V	α	K
10	0·866	1·68
20	0·890	1·61
100	0·942	1·54
500	0·974	1·61
1000	0·980	1·54

Van 't Hoff[2] shows that equally good results are obtained from the equation

$$\frac{\alpha^3}{(1-\alpha)\, V^{\frac{1}{2}}} = K, \quad \text{or} \quad \frac{\alpha^3}{(1-\alpha^2)V} = K'.$$

Thus for silver nitrate at 25° the comparable constants are:

V	α	K_1 (Rudolphi)	K' (Van 't Hoff)
16	0·828	1·00	1·11
32	0·875	1·16	1·16
64	0·899	0·92	1·06
128	0·926	1·06	1·07
256	0·947	1·10	1·08
512	0·962	1·14	1·09

[1] *Zeits. phys. Chem.* XVII. 385 (1895).
[2] *Zeits. phys. Chem.* XVIII. 300 (1895).

Van 't Hoff's equation can be deduced by the kinetic method on the assumptions that the number of molecules dissociating is proportional to the square of the whole number of undissociated molecules, and that the number of ions recombining is proportional to the cube of the whole number of ions, the equation of equilibrium being

$$\frac{C_2^3}{C_1^2} = K'.$$

Kohlrausch points out that Van 't Hoff's formula, if written in the form

$$\frac{C_2^3}{C_1^2} = \text{constant}, \quad \text{or} \quad \frac{C_2}{C_1^{\frac{2}{3}}} = \text{constant},$$

and divided on each side by $C_1^{\frac{1}{3}}$, becomes

$$\frac{C_2}{C_1} = \frac{\text{constant}}{C_1^{\frac{1}{3}}}.$$

$C_1^{\frac{1}{3}}$ denotes the average nearness of the molecules, so that, if r be the average distance between them, we get the very simple relation

$$\frac{C_2}{C_1} = r \times \text{constant},$$

the ratio between the ionic and the molecular concentrations being proportional to the average distance between the undissociated molecules.

Turning from these empirical relations, let us consider once more Ostwald's original dilution equation, which extends the chemical law of mass action to the dissociation of electrolytes. In deducing the law by the application of thermodynamics, the restriction to dilute systems is necessary, in order that the reacting particles may be beyond each other's sphere of influence, and the change with dilution of available energy be thus independent of the nature of the solvent. Now, as we pointed out on p. 324, on the hypothesis that chemical forces are of electrical origin, the influence of a dissociated ion will extend far beyond the range at which the forces between the non-dissociated molecules cease to be sensible. A solution containing dissociated ions will therefore fail to show the properties of dilute matter at a much less concentration than

will the solution of a non-electrolyte. It is not surprising, therefore, that the dilution law does not hold at the concentrations at which it is tested. It is possible that it would only be applicable at dilutions so great that most solutions of strong electrolytes would be almost completely dissociated; in fact, as already stated, it is possible that, as the concentration increases, the electric forces between the dissociated ions would become sensible sooner than any combination could occur. In the case of weakly dissociated bodies, like acetic acid, the number of ions at moderate concentrations is enormously smaller than for strong acids and salts; it is possible, also, that the presence of a large quantity of undissociated solute affects the properties of the medium and diminishes the electric forces between the separated ions. Such solutions, therefore, show the phenomena of dilute systems at comparatively high concentrations, and conform to the dilution law.

The application of the mass law as hitherto considered is concerned only with substances which dissociate into two ions. For salts or acids, which, like barium chloride or sulphuric acid, may be expected to give three ions, equation (62) on p. 340 becomes

$$\frac{C_2^3}{C_1} = K,$$

and we get

$$\frac{\alpha^3}{V^2(1-\alpha)} = K,$$

for the dilution law. If α is small we may write

$$\alpha = \sqrt[3]{V^2K} \quad \text{.....(67).}$$

In the case of weak polybasic acids, succinic for example, the ionization at high concentrations conforms to the law for monobasic acids, and varies with the square root of the dilution in accord with equation (66) on p. 341. This behaviour indicates that the ions are H' and HA', where A denotes the acid group, and the dashes the valency of the ion. When about half the molecules are dissociated, some begin to produce three ions, and, at greater dilutions, the dissociation becomes normal in agreement with equation (67) above, indicating H', H', and A'' as the ions. From strongly ionized bodies three ions are

usually formed at more moderate dilutions, as shown by the conductivity and the depression of the freezing point, though, as we have seen, some of them may be linked with solute or solvent molecules to form complex ions. For these bodies, as for the corresponding binary compounds, the theoretical dilution law fails.

Equilibrium between electrolytes.

When solutions of two electrolytes are mixed, there will, in general, be a change in the amount of ionization in both. For particular concentrations of bodies which conform to the dilution law, however, we can show that no such change occurs, and the solutions can be mixed without affecting the number or nature of the ions, or the mean conductivity. Any two solutions which fulfil these conditions were called by Arrhenius isohydric. Let us, as the simplest case, consider two simple electrolytes which possess one ion in common, such as two acids HA_1 and HA_2. Let the coefficients of ionization be α_1 and α_2, and the dilutions V_1 and V_2 respectively. Then, for the two solutions

$$\frac{\alpha_1^2}{(1-\alpha_1)V_1} = K_1 \quad \text{and} \quad \frac{\alpha_2^2}{(1-\alpha_2)V_2} = K_2.$$

If the solutions be isohydric, we can mix them without changing the ionizations; the total volume becomes $V_1 + V_2$, and the number of hydrogen ions $\alpha_1 + \alpha_2$. For the acid HA in the mixed solution, since the number of A ions remains unchanged at α_1, we have by equation (63) on page 340,

$$\frac{(\alpha_1+\alpha_2)\alpha_1}{(1-\alpha_1)(V_1+V_2)} = K_1.$$

Dividing this equation by the first, we get

$$\frac{(\alpha_1+\alpha_2)V_1}{(V_1+V_2)\alpha_1} = 1, \quad \text{or} \quad \frac{\alpha_1+\alpha_2}{\alpha_1} = \frac{V_1+V_2}{V_1}.$$

Thus

$$\frac{\alpha_1}{\alpha_2} = \frac{V_1}{V_2}, \quad \text{or} \quad \frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2} \quad \ldots\ldots\ldots\ldots\ldots(68).$$

Now α_1/V_1 and α_2/V_2 are the respective concentrations of the hydrogen ions in the two isohydric solutions HA_1 and HA_2. It follows, then, that solutions of electrolytes containing a common

ion are isohydric when the concentration of the common ion in the different solutions is the same.

Two solutions with a common ion will so act on each other when mixed that they become isohydric, for then alone will the undissociated part of each be in equilibrium with the dissociated ion common to both.

In deducing this result, the dilution law has been used; the investigation therefore only applies in the case of electrolytes which conform to that law. Nevertheless, similar principles probably hold in other cases, and we may use our conclusion to qualitatively elucidate the interaction of solutions of any two acids. If the solution of a strong acid like hydrochloric be mixed with that of a weak acid like acetic, equilibrium can only occur when the two acids are isohydric and the concentration of the hydrogen ions the same for both. In order to secure this condition, it is necessary that a large amount of the feebly dissociated acetic acid, and a small amount of the highly dissociated hydrochloric, should exist. Now when dilute hydrochloric acid is mixed with dilute sodium acetate, acetic acid is formed, and this process continues till the two acids are isohydric, and the dissociated hydrogen ions in equilibrium with both. A large quantity of undissociated acetic acid must therefore be formed, and consequently most of the acetate be decomposed. This replacement of a weak acid by a strong one is a matter of common observation in the chemical laboratory. As indicated on p. 336 however, it must be noticed that the relative strengths of two acids can only be determined when both remain within the sphere of action; if one of them is removed by precipitation or evaporation, it will be completely replaced, irrespective of the relative strengths.

The theory of isohydric solutions can also be applied to investigate the effect on the solubility of one salt of adding to its solution a quantity of another salt containing an ion common to both. Nernst has pointed out[1] that in all likelihood the equilibrium between a solid salt and its solution is primarily an equilibrium between the crystals and the undissociated dissolved molecules, which on the other hand, are themselves

[1] *Zeits. phys. Chem.* IV. 372 (1888).

in equilibrium with the dissociated ions. Under constant external conditions, therefore, we may conclude that the amount of the undissociated solute present in the liquid is not changed by adding more of either of its ions. In order to simplify the theory as much as possible, let us consider the case of a sparingly soluble salt, silver bromate for example[1]. The concentration of the silver ions can be increased by adding a soluble silver salt, and that of the bromate ions by adding a soluble bromate. Let us add a quantity of silver nitrate. The quantity of undissociated silver bromate is unchanged, and must still be in equilibrium with the silver and bromate ions. According to the mass law, the product of the concentrations of these two ions must be equal to the concentration of the undissociated salt multiplied by a constant; in this case the product must itself be constant. By increasing the number of the silver ions, then, the concentration of the bromate ions must be diminished in the same ratio. A bromate ion can only be precipitated in company with some positive ion; thus silver bromate, formed by the combination of its ions, is deposited to restore equilibrium. The effect of adding the silver nitrate therefore is to reduce the solubility of the silver bromate proportionally to the quantity of nitrate added. The effect of a soluble bromate is exactly similar, and the solubility of the silver bromate is lowered to the same extent as by an equivalent quantity of silver nitrate.

This account of the subject has been quantitatively confirmed[1]. A solution of silver bromate, saturated at 24°·5, contains 0·0081 gram-equivalents per litre. Assuming that the salt is practically completely dissociated, the product of the concentrations of the two ions is $0{\cdot}0081^2$, or 0·0000656. To such a solution, a quantity of silver nitrate was added sufficient to give a 0·0085 normal solution of the nitrate when dissolved in the volume of water which contained the bromate. Assuming complete dissociation for the silver nitrate also, let us calculate x, the total quantity of silver bromate which remains dissolved. The concentration

[1] The details of the calculations which follow are taken from Walker's *Physical Chemistry* (1899), p. 294.

of the bromate ions is x, and that of the silver ions $0{\cdot}0085 + x$. Thus,

$$(0{\cdot}0085 + x)\, x = 0{\cdot}0000656,$$

whence

$$x = 0{\cdot}0049.$$

An experimental measurement showed that the solubility was actually reduced from 0·0081 to 0·0051 normal. If the calculation be corrected for the changes in the ionization of the salts indicated by conductivity determinations, the theoretical number becomes 0·00506, even nearer to the observed result.

Two sparingly soluble salts, shaken up with the same quantity of water, each reduce the solubility of the other. The saturated solutions of thallium chloride and thallium thiocyanate have concentrations of 0·0161 and 0·0149 normal respectively. If x and y denote the solubility of the two salts respectively each in presence of the other, the concentration of the Cl ions is x and that of the SCN ions is y, while the sum $x+y$ gives the concentration of the thallium ions. We thus obtain

$$x\,(x+y) = 0{\cdot}0161^2$$

and

$$y\,(x+y) = 0{\cdot}0149^2$$

whence we calculate that x is 0·0118, and y is 0·0101; direct experiment gives 0·0119 and 0·0107 for the same quantities. These results justify the use of the principles here involved in such cases as the electromotive force of concentration cells, etc., examples of which we have already considered (pp. 253, 254). Owing to the failure of the mass law for solutions of strong electrolytes, we should expect these results, which depend on the same principles, to be limited in their application. The concordance between theory and experiment in the cases given, indicates that, for very slightly soluble salts, the theory is justified. This result is of great interest, for it shows that at great dilution, when the ions are beyond each other's spheres of influence, the mass law holds for strong electrolytes. Attempts have been made to use this solubility method to determine the ionization of the salt added, but consistent results are obtained only when the salt precipitated is very slightly soluble[1].

[1] Arrhenius, *Zeits. phys. Chem.* XI. 391 (1893).

These principles are often used in the chemical laboratory to precipitate salts from solution in a state of purity. Thus sodium chloride can be separated from a strong solution by the addition of hydrochloric acid, a very soluble substance also containing chlorine ions. The product of the concentrations of the ions of sodium and chlorine exceeds the equilibrium value, and salt is precipitated.

The problem of the equilibrium of two electrolytes which have no common ion is much more complicated. When, for example, the solutions of two salts M_1A_1 and M_2A_2 are mixed, the final system will contain the ions $\overset{+}{M}_1$, $\overset{+}{M}_2$, $\overset{-}{A}_1$ and $\overset{-}{A}_2$, together with undissociated molecules of M_1A_1, M_2A_2, M_1A_2 and M_2A_1; the equilibrium to be investigated is that which holds between all these bodies under the conditions of the experiment. Of the four salts, any two which contain a common ion can be treated by the methods already adopted. Thus a solution of M_1A_1 can be made isohydric with one of M_1A_2. But the same solution of M_1A_1 can be made isohydric with M_2A_1 with regard to the other ion, and the solution of M_1A_2 can be made isohydric with that of M_2A_2. The conditions which must hold between the volumes of the four isohydric solutions to secure that their equilibrium is not disturbed when they are mixed, can be investigated on the assumption that they all conform to Ostwald's dilution law. For one of them, say M_1A_1, we have with the usual notation,

$$\frac{\alpha_1^2}{(1-\alpha_1)V_1} = K.$$

If all the solutions be now mixed without change of equilibrium, the number of the M_1 ions will increase in the ratio of $(V_1+V_2)/V_1$, where V_2 is the volume of the isohydric solution of M_1A_2 in which the concentration of the M_1 ions must be the same. The volume in which the M_1 ions are now contained is, however, $V_1+V_2+V_3+V_4$, so that the concentration of the M_1 ion is

$$\alpha_1 \cdot \frac{V_1+V_2}{V_1} \cdot \frac{1}{V_1+V_2+V_3+V_4} = \frac{\alpha(V_1+V_2)}{V_1(V_1+V_2+V_3+V_4)}.$$

Similarly the number of A_1 ions is increased in the ratio $(V_1 + V_3)/V_1$, and its concentration becomes

$$\frac{\alpha(V_1 + V_3)}{V_1(V_1 + V_2 + V_3 + V_4)},$$

where V_3 and V_4 are the volumes of the isohydric solutions of M_2A_1 and M_2A_2 respectively. The new equilibrium of the salt M_1A_1 will thus be given by the equation

$$\frac{\dfrac{\alpha(V_1 + V_2)}{V_1(V_1 + V_2 + V_3 + V_4)} \cdot \dfrac{\alpha(V_1 + V_3)}{V_1(V_1 + V_2 + V_3 + V_4)}}{\dfrac{1 - \alpha}{V_1 + V_2 + V_3 + V_4}} = K.$$

Hence by the dilution law

$$\frac{\alpha^2(V_1 + V_2)(V_1 + V_3)}{(1 - \alpha)V_1^2(V_1 + V_2 + V_3 + V_4)} = \frac{\alpha^2}{(1 - \alpha)V_1}.$$

Thus

$$\frac{(V_1 + V_2)(V_1 + V_3)}{V_1(V_1 + V_2 + V_3 + V_4)} = 1,$$

which reduces to

$$V_1 V_4 = V_2 V_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (69),$$

an equation giving the relation which must hold between the volumes of the four isohydric solutions, in order that there should be no disturbance in equilibrium when mixture occurs. In words, we may say that the products of the volumes of such pairs of solutions as contain no common ion must be equal to each other. The solutions were all isohydric; that is, they had the same ionic concentration. The equilibrium condition, therefore, means that the total number of ions in each of the four solutions must be the same. In the chemical equilibrium

$$M_1A_1 + M_2A_2 \rightleftarrows M_1A_2 + M_2A_1,$$

let us call the total masses of the four substances m_1, m_2, m_3 and m_4 respectively, and their coefficients of ionization α_1, α_2, α_3 and α_4. For equilibrium on mixing, and therefore when equilibrium is reached in any case, our relation becomes

$$m_1\alpha_1 \cdot m_4\alpha_4 = m_2\alpha_2 \cdot m_3\alpha_3.$$

This result is evidently an expression of the mass law, but it shows that the active mass of one of the substances we are considering is not its total mass, but only the fractional quantity which is dissociated into electrolytic ions.

We have seen that the solubility of a salt may be reduced by the addition of an electrolyte containing one of the same ions. On the other hand, under certain conditions, the addition of an electrolyte may increase the solubility of a precipitate or other sparingly soluble body. For example, the small quantity of calcium tartrate which dissolves in water is highly dissociated. If hydrochloric acid be added, tartaric acid is produced, which, in presence of the ions of calcium chloride, etc., is only slightly dissociated. The concentration of the tartrate ions is therefore much reduced, the ionic product falls below the saturation value, and more calcium tartrate is dissolved. Further applications of this theory of chemical equilibrium in electrolytes will be found in Arrhenius' paper, and in most books on Physical Chemistry.

Thermal properties of electrolytes.

When two neutral salt solutions are mixed, there is, in general, neither evolution nor absorption of heat. This experimental result has been formulated in what is known as Hess' law of thermo-neutrality. The dissociation theory indicates that, when all four possible salts are fully ionized, and consequently exist in solution in a dissociated condition, no appreciable change can occur on mixing, and no thermal phenomena can appear. If one of the reagents or one of the products of the action is only slightly dissociated, a separation of molecules or a combination of ions will take place when the solutions are mixed, and heat will be developed or absorbed.

In the same way, the remarkable conclusion at which Thomsen arrived from his experiments on the heat of neutralization of acids and bases may be explained. He found that when a strong acid reacted with an equivalent quantity of a strong base in dilute solution, the heat evolved was always about 13,700 or 13,800 calories per gram-equivalent, whatever the acid and base used. The dissociation theory considers the reaction, for example, between hydrochloric acid and potash to be represented by the equation

$$\overset{+}{H} + \overset{-}{Cl} + \overset{+}{K} + \overset{-}{OH} = \overset{+}{K} + \overset{-}{Cl} + H_2O.$$

The ions K and Cl suffer no change, but the H of the acid and the OH of the alkali unite to form water, which, being present in a relatively enormous quantity, is only dissociated to an exceedingly small amount. An exactly similar process occurs when any strongly ionized acid acts on any strongly ionized base, and it is thus evident why, in such cases, the heat evolution should remain about constant.

The law of thermo-neutrality, and the constancy of the heat of neutralization of strong acids and bases have been explained in ways which do not involve the dissociation hypothesis. Crompton[1], for example, points out that the experiments of Thomsen prove that, when hydrogen is replaced in a monomolecular organic compound by any radicle, the heat evolved is independent of the group with which the hydrogen was originally united. Extending this result to inorganic bodies, it might be that the heat of replacement of hydrogen in the acid is equal and of opposite sign to that of the replacement of hydroxyl in the base. The total heat of neutralization would then be zero, except for the thermal change accompanying the alteration in state of the elements of water, which before the action exist as parts of diluted foreign molecules, and after the action are added to the liquid solvent as part of itself. The heat evolution, then, would be a thermal value analogous to the heat of condensation of water from vapour to liquid, and the law of thermo-neutrality of reacting salts would hold good when no water is formed. Such a theory of course expresses the isolated facts to explain which it was framed, but it cannot connect the thermal and electric properties of solutions.

In reactions with the weaker acids and bases, the ionization of which is less complete, the heat evolved will diverge from the normal value, for the salts produced are usually more dissociated, and ions will be formed during the process. For instance, in the solutions used by Thomsen, sulphuric acid is only about half dissociated, and shows a heat of neutralization higher than the normal, so that heat must be evolved when it is resolved into its ions.

[1] *Chem. Soc. Journ. Trans.* LXXI. 951 (1897).

Heat of ionization.

Since the energy associated with a quantity of substance when ionized is different from that associated with it when in the normal chemical state, the heat of formation in aqueous solution of the molecule of an electrolyte from its ions will generally be different from that evolved when it is produced from its non-ionized elements.

The heat of ionization of an electrolytic substance can be calculated by an application of the principles of thermodynamics. In the deduction of the mass law of chemical equilibrium on p. 339, it was shown that the change of available energy of a system per molecule of isothermal reaction could be expressed in the form

$$\delta\psi = n_1 a_1 + n_2 a_2 + \ldots + RT\,(\log\, b_1^{n_1} b_2^{n_2} \ldots\, C_1^{n_1} C_2^{n_2} \ldots).$$

Thus $$\delta\psi = \delta\psi_0 + RT \log K',$$

where $\delta\psi_0$ is a standard of reference, and K' is $b_1^{n_1} b_2^{n_2} \ldots K$. As the condition of equilibrium at each temperature, $\delta\psi$ must vanish, so that

$$\delta\psi = -RT \log K'.$$

By partial differentiation, for unaltered materials,

$$\frac{\partial}{\partial T}\left(\frac{\delta\psi}{T}\right) = \frac{\partial}{\partial T}\left(\frac{\delta\psi_0}{T}\right) = -R\frac{\partial}{\partial T}\log K'$$

$$= -R\frac{\partial}{\partial T}\log K \ldots\ldots\ldots\ldots\ldots\ldots\ldots (70),$$

a result which is independent of the unknown term ψ_0.

In the free energy equation (p. 29)

$$\psi = \epsilon + T\frac{\partial\psi}{\partial T}$$

ψ and ϵ refer to changes in the free and internal energy respectively, so that ψ is equivalent to $\delta\psi$ above. Now the heat λ absorbed by the system is

$$\lambda = \epsilon - \psi = -T\frac{\partial\psi}{\partial T} = -T^2\frac{\partial}{\partial T}\left(\frac{\psi}{T}\right).$$

Hence from (70) we get

$$\lambda = RT^2\frac{\partial}{\partial T}\log K \ldots\ldots\ldots\ldots\ldots\ldots (71)$$

as the heat absorbed by the system per molecule of isothermal reaction. This expression, due to Van 't Hoff, is a more general form of equation (17) on p. 115, which gives the heat of

solution of a substance in terms of the temperature coefficient of solubility. Equation (17) can of course be obtained from (71).

If we make the assumption that the heat of reaction is independent of the temperature, which will restrict our result to somewhat small temperature ranges, we may integrate this new equation and obtain

$$\log \frac{K_2}{K_1} = \frac{\lambda}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (72).$$

These results apply to chemical changes in any dilute system, and may therefore be used to calculate the heat of ionization per gram-molecule when the constants K_1 and K_2 are known for two neighbouring temperatures.

The coefficient of dissociation of aqueous solutions is generally found to decrease as the temperature rises; and by experimentally determining its value for different temperatures and calculating the rate of variation, Arrhenius[1] has measured the heats of formation of various molecules from their ions by means of this equation. It is important to observe that his results only apply to solutions in water, and that, for the strongly dissociated bodies, for which Ostwald's dilution law fails, it is not to be expected that this theory, depending on similar principles, should lead to true results for the heats of ionization. The numbers for strongly dissociated bodies in the following table are calculated from observations on decinormal solutions.

Substance		λ at 21°·5	λ at 35°
Acetic acid	CH_3COOH	+ 28	− 386
Propionic acid	C_2H_5COOH	− 183	− 557
Butyric acid	C_3H_7COOH	− 427	− 935
Phosphoric acid	H_3PO_4	−2103	−2458
Hydrofluoric acid	HF	−3200	−3549
Hydrochloric acid	HCl		−1080
Nitric acid	HNO_3		−1362
Soda	$NaOH$		−1292
Potassium chloride	KCl		− 362
Barium chloride	$BaCl_2$		− 307
Sodium butyrate	C_3H_7COONa		+ 547

[1] *Zeits. phys. Chem.* IV. 96 (1889); IX. 339 (1892).

From this table, by adding to the heat of formation of water from its ions that evolved by the completion of the dissociation of the acid, Arrhenius has calculated the total heats of neutralization of soda by different acids.

Substance	Calculated	Observed
Hydrochloric acid HCl	13447	13740
Hydrobromic „ HBr	13525	13750
Nitric „ HNO_3	13550	13680
Acetic „ CH_3COOH	13263	13400
Phosphoric „ H_3PO_4	14959	14830
Hydrofluoric „ HF	16320	16270

In the case of strongly dissociated substances, the number of molecules undissociated is so small that the variation from the normal value of the heat of neutralization is too slight to test the equation by experiment. For the weak acids, phosphoric, acetic, and hydrofluoric, which conform to the dilution law, the concordance is seen by the table to be satisfactory.

From equation (71) on p. 354, it follows that, if the heat of formation is negative, that is, the heat of dissociation positive, the value of $\partial (\log K)/\partial T$ is also negative, and the dissociation must become less with increasing temperature. The conductivity is dependent on two factors, (1) the dissociation, and (2) the frictional resistance offered by the solution to the passage of the ions through it. If we call the reciprocal of this resistance the ionic fluidity of the solution, the molecular conductivity will be proportional to the dissociation and to the ionic fluidity. At great dilution the dissociation is complete, and the ions are so far apart that no change in temperature can affect the state of dissociation. Any alteration in conductivity with change of temperature must then be due to an alteration in fluidity, and the temperature coefficient of fluidity can be determined by measuring the temperature coefficient of conductivity at a dilution so great that the molecular conductivity has reached its limiting value. Now the table on p. 355 shows that the heats of formation from their ions of the substances examined have a greater negative

value at the higher temperature. From equation (71) it follows that the rate of decrease of dissociation with increase of temperature must therefore increase as the temperature rises. If the temperature coefficient of fluidity either decreases with rise of temperature, keeps constant, or increases more slowly than the negative coefficient of dissociation, it is clear that a maximum conductivity must be reached at a certain temperature, beyond which any further heating will decrease the dissociation more than it increases the fluidity, and so, on the whole, diminish the conductivity.

Arrhenius calculated, by deductions from the equation, that solutions of the two slightly dissociated bodies, hypophosphoric and phosphoric acids, should have maximum values for the conductivity at 57° and 78° respectively. He then experimentally determined their conductivities at different temperatures, and actually found maxima at 55° and 75°. Sack[1], by measuring the conductivity of copper sulphate solutions in closed vessels, found a maximum at 96° for a 0·64 per cent. solution; calculation by Arrhenius' method gives 99° for a solution of this concentration.

The heat of ionization hitherto considered is the heat evolved when the molecule of a salt or acid is dissociated into its ions in aqueous solution. The determination of the heat change associated with the formation of an equivalent weight of ions during the process of solution of a metal is a different problem, and Ostwald[2] has attacked it on the assumptions that the single potential difference at the interface between a metal and a solution is known, and that the Gibbs-Helmholtz equation

$$E = \lambda + \theta \frac{dE}{d\theta}$$

is applicable not only to the whole cell, but also to each individual surface of contact within it. E is then the single potential difference, and λ the total heat effect at the electrode, which measures the heat of ionization generated by the passage of the metal into the ionic state. From this point of view,

[1] *Wied. Ann.* XLIII. 212 (1891).

[2] *Lehrbuch*, p. 955.

such thermo-chemical data as the heat of precipitation of copper from its solution by zinc, are always the sums or differences of two heats of ionization, and if one heat of ionization is known, others may be calculated from thermo-chemical values. The following are some of the heats of ionization given by Ostwald:

	Per gram-atom	Per gram-equivalent		Per gram-atom	Per gram-equivalent
Potassium	+612	+612	Iron (change from ferrous to ferric ions)	−121	−121
Zinc	+331	+166	Lead	− 14	− 7
Cadmium	+165	+ 83	Copper	−177	− 89
Thallium	+ 8	+ 8	Silver	−264	−264
Iron (ferrous)	+202	+101	Mercury	−207	−207

The thermal unit is 100 calories. The results depend on the presumed correct determination of single potential differences by the use of capillary electrometers and dropping electrodes.

Dissociation of water.

The conductivity of carefully distilled water is very small, and it can therefore only be dissociated to a very slight extent. The best water which can be prepared by distillation in presence of air has a conductivity of about $0{\cdot}7 \times 10^{-6}$ measured in reciprocal ohms across a centimetre cube. Kohlrausch and Heydweiler[1] have distilled water in a vacuum and collected it directly in a resistance cell, which had been kept for ten years full of distilled water in order to dissolve all the soluble constituents of the glass; in this manner they obtained water with a conductivity of $0{\cdot}015 \times 10^{-6}$ at 0°, and $0{\cdot}043 \times 10^{-6}$ at 18°. From the experimental results alone it is impossible to tell whether the slight trace of conductivity which remains is due to residual impurities or to ionization of the water itself, but an examination of the question may be made from the thermodynamic standpoint. The constant heat of neutralization of

[1] *Wied. Ann.* LIII. 209 (1894). In the paper the conductivity is expressed in terms of that of mercury; the numbers have here been reduced to reciprocal ohms across a centimetre cube.

strong acids and alkalies is due on the dissociation theory to the combination of the ions of water, and therefore gives for the heat of ionization per gram-molecule a value of 13,700 calories at 18°. Van 't Hoff's equation (71)

$$\frac{\partial}{\partial T}\log K = \frac{\lambda}{RT^2}$$

in combination with the dilution law for weak binary electrolytes which shows, as on p. 341, that K is α^2/V, leads to the result

$$\frac{1}{\alpha}\frac{\partial \alpha}{\partial T} = \frac{\lambda}{2RT^2},$$

from which the temperature coefficient of the dissociation can be calculated. The conductivity, in accordance with Kohlrausch's theory, depends on the product of the dissociation and the sum of the ionic mobilities, which varies with the ionic fluidity. The ionic mobilities of the hydrogen and hydroxyl were found by experiments on 0·001 normal solutions of potash, hydrochloric acid, and potassium chloride, to vary with temperature in accordance with the equation

$$10^4\,(u+v) = 352 + 8{\cdot}3t,$$

t being the temperature on the Centigrade scale. At this great dilution the ionization of the solutes may be taken as complete, so that the influence of temperature on conductivity is due to its effect on fluidity alone. The total temperature coefficient of conductivity of pure water calculated from these data is 0·0581. The experiments showed that, as continual purification of the water lowered its conductivity from $0{\cdot}29 \times 10^{-6}$ to $0{\cdot}043 \times 10^{-6}$, the temperature coefficient of its conductivity increased from 0·027 to 0·0532. It was hence estimated that the temperature coefficient would rise to the thermodynamic value when the conductivity had sunk to $0{\cdot}0386 \times 10^{-6}$ at 18°. This result, then, was taken to be the conductivity of pure water. It will be seen that about ten per cent. of the conducting power of Kohlrausch's best water is due to impurities. From the conductivity of pure water, its dissociation can be calculated; and Kohlrausch's values indicate that the number of gram-equivalents dissociated per litre is

$0{\cdot}35 \times 10^{-7}$ at 0°, $0{\cdot}80 \times 10^{-7}$ at 18°, $1{\cdot}09 \times 10^{-7}$ at 26°, and $2{\cdot}48 \times 10^{-7}$ at 50°. Thus a cubic metre of water at 18° contains about 1·4 milligrams of dissociated molecules, or 0·08 milligrams of hydrogen ions. It may be observed that the ionic mobilities assumed in this investigation are the maximum values. Now at extreme dilution the equivalent conductivity of acids and alkalies diminishes, and it is possible that this phenomenon may somewhat affect the result of the calculation.

Another value for the dissociation of water has been obtained by examining its influence on chemical reaction velocities. Methyl acetate and water form methyl alcohol and acetic acid at a rate proportional to the number of hydroxyl ions present in the solution. Wijs[1] used this reaction to measure the dissociation of water; he prepared an aqueous solution of methyl acetate carefully freed from acid or other impurity, and titrated it at intervals with standard alkali to measure the amount of acetic acid produced. The acid, as it is formed, retards the action, so that it is necessary to estimate the rate of transformation at the beginning of the process. The concentration of the dissociated ions appeared to be about $1{\cdot}2 \times 10^{-7}$ gram-equivalents per litre at 25°.

A third method of estimating the dissociation of pure water has been used by Ostwald[2]. A plate of spongy platinum in contact with hydrogen and an electrolyte acts as a hydrogen electrode, and if two such electrodes are arranged, one in an acid and the other in an alkali, the system may be treated as a concentration cell with regard to the hydrogen ions. In a normal acid solution, owing to the incomplete ionization, the concentration of the hydrogen ions is about 0·8, so that the concentration of the same ions round the alkali electrode can be calculated from the logarithmic formula [(48) p. 248]

$$E = \frac{riRT}{qy} \log \frac{P_2}{P_1}$$

with the notation there indicated. The electromotive force of the cell is complicated by the potential difference of contact

[1] *Zeits. phys. Chem.* XI. 492; XII. 514 (1893).
[2] *Zeits. phys. Chem.* XI. 521 (1893).

between the two solutions, as was pointed out by Nernst[1]; and at 18° the corrected value is given as 0·81 volt. Putting in this number, we may consider the effect of the liquid contact to be eliminated and assume the transport ratio r to be 0·5, and Van 't Hoff's factor i to be 2. The gram ionic charge q is 9644 C.G.S. units, and y the valency of the ions is 1. Transforming to common logarithms, the equation then gives

$$0{\cdot}81 = 0{\cdot}0575 \log_{10} \frac{P_2}{P_1},$$

or

$$\frac{P_2}{P_1} = 10^{14}.$$

Since P_2 is 0·8, P_1 the concentration of the hydrogen ions in the alkali solution is $0{\cdot}8 \times 10^{-14}$. By the mass law we know that the product of the two ionic concentrations divided by the concentration of the undissociated water should be a constant. The water is present in large excess and its quantity may be taken as unalterable, so that the ionic product itself is constant, and will have the same value in pure water as in the solution of alkali, namely $0{\cdot}64 \times 10^{-14}$. In pure water the concentrations of the hydrogen and hydroxyl ions must be equal, and the dissociated fraction is therefore $0{\cdot}8 \times 10^{-7}$ gram-equivalents per litre. This exact agreement with Kohlrausch's result may not be justified by the approximate nature of the calculations, but it shows that values of the same order are obtained in the two ways.

The function of the solvent.

The differences which exist between the conductivities of the same substance when dissolved in different solvents show that the power of conducting a current depends on the nature of the solvent as well as on that of the solute. The conductivity depends on two factors, the ionization and the ionic fluidity of the liquid, and, to secure ready conduction, both these properties must have high values.

A suggestion made independently by J. J. Thomson[2] and Nernst[3] may possibly explain the property possessed by certain

[1] *Zeits. phys. Chem.* XIV. 155 (1894).
[2] *Phil. Mag.* [5] XXXVI. 320 (1893).
[3] *Zeits. phys. Chem.* XI. 220 (1893).

solvents of ionizing substances dissolved in them. If the forces holding the ions together in a molecule are electrical in their nature, they will be much weakened by immersing the molecule in a medium of high specific inductive capacity. The effect can be illustrated by considering the influence of a mass of conducting material placed near two little particles charged with opposite kinds of electricity. The result of the presence of the conductor can be represented by imagining that electrical images of opposite sign are formed near the charges just inside the conductor. The external forces due to the charged particles are reduced, and thus their attraction for each other may be so much diminished that separation may occur. The effect of an insulator of high dielectric constant is similar in kind, though rather less in magnitude; and, other things being equal, the relative ionization powers of solvents should be proportional to their specific inductive capacities.

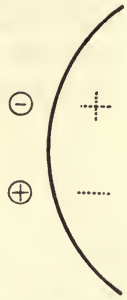


Fig. 65.

Some results, which, as far as they go, support this conclusion for solutions in water, methyl alcohol, and ethyl alcohol, have been given by the present writer[1]. The specific inductive capacities of the three solvents are, according to Tereschin: water, 83·7: methyl alcohol, 32·65: ethyl alcohol, 25·8. If we suppose provisionally that the resistances offered by these solvents to the motion of the ions are in about the same ratios as their viscosities, we must divide these numbers by 100, 63 and 120, respectively. We then get for the theoretical ratio of the conductivities,

Water 100 Methyl Alcohol 63 Ethyl Alcohol 26.

An investigation by Völlmer showed that, for many salts, the ratio of the conductivities in the three solvents was

Water 100 Methyl Alcohol 73 Ethyl Alcohol 34.

It seems probable, then, that the specific inductive capacity and the viscosity are important factors in determining the relative ionization powers of solvents. More recently an attempt was made to ionize water by dissolving it in different

[1] *Phil. Mag.* xxxviii. 392 (1894).

solvents. The object of the work was not attained, but it was shown by Novak and by the writer that, for mixtures of water with excess of formic acid, of which the dielectric constant is about 62, the conductivity curve is more like that of an electrolyte in water than it is when substances of lower dielectric constant, such as acetic acid, are used as solvent[1]. Slight dissociation of water dissolved in methyl alcohol has been found by Carrara, who shows that extremely dilute solutions conform to the mass law[2].

On the other hand there seem to be many exceptions to this rule of concordance between ionizing power and dielectric constant. Liquefied ammonia and sulphur dioxide dissolve salts to form solutions which conduct well, but both solvents have low specific inductive capacities. Other exceptions have been given by Kahlenberg and Schlundt[3]. In view of the well-known fact that many aqueous solutions, such as those of ammonia and acetic acid, are only ionized to a very small extent, it is evident that no such rule as that under discussion can be universally true. Influences due to the specific nature both of solvent and solute must prevent any complete generalization. The fundamental idea of the Thomson-Nernst theory is, however, a valuable advance towards the explanation of the ionizing power of solvents.

It is worthy of remark that, as well as reducing the forces between ions, the conducting body in Figure 65 will attract each ion to itself. The same thing would occur in a solvent of high specific inductive capacity. When the forces between two ions have been loosened, a slight collision with other molecules, or with molecules of the solvent, may suffice to cause dissociation; the liberated ions may be annexed by the solvent, and loose compounds formed. The ions, being dissociated from each other and readily passed on from one particle of the solvent to the next, would then be able to work their way through the liquid under the action of the external electric forces.

[1] *Phil. Mag.* [5] XLIV. 1 and 9 (1897).
[2] *Gazz. Chim. Ital.* XXVII. 1. 422 (1897).
[3] *Journ. Phys. Chem.* v. 382 and 503 (1901).

Brühl[1] has pointed out that since oxygen can act as a quadrivalent as well as a divalent element, water and other substances containing it must be looked on as unsaturated compounds. Hence arise their high dielectric constants, great powers of ionization and readiness of combination. The ions in such substances may be supposed to be loosely and distantly connected, so that the electric moment of a molecule is great. Such a molecule when in solution will come under a powerful influence from any ion it encounters, and is therefore easily dissociated. Alcohols, ketones, ethereal salts, and acids also contain oxygen, and their dissociating power decreases as their molecular weight rises and their content of oxygen diminishes. The valency of nitrogen, like that of oxygen, can vary, and nitrogen compounds, nitriles, etc., give conducting solutions. Hydrocarbons and other saturated substances have little or no dissociating power. Dutoit and Aston[2] have further remarked that the liquid solvents considered above, when examined by the capillary methods of Ramsay and Shields and otherwise, are found to consist of polymerized molecules. It is probable that all these properties are connected, though again exceptions to any law of exact correlation have been indicated by Kahlenberg.

Hydrolytic dissociation.

Solutions of salts which are strong electrolytes give a neutral reaction; but a salt such as chloride or nitrate of copper or zinc, containing a strong acid and a weak base, is found to give an acid solution, or if the base is strong and the acid weak, as in sodium carbonate or potassium cyanide, the reaction of the solution is alkaline. These results are explicable if we remember that water is to a slight extent dissociated, and may thus act either as a weak acid in virtue of its hydrogen ions or as a weak base because it contains hydroxyl. When a salt MA is dissolved in water, the reversible decomposition known as hydrolysis

$$MA + HOH = MOH + HA$$

[1] *Ber.* XXVIII. 2866 (1895); *Zeits. phys. Chem.* XVIII. 514 (1895); XXVII. 319 (1898).

[2] *Compt. rend.* CXXV. 240 (1897).

may produce a non-electrolytic dissociation of the salt. This process is always possible, and must therefore occur to some degree in every case. The condition of equilibrium, equation (69) on p. 351, shows that the product of the ionic concentrations must be the same on each side of the equation. The ionic concentration of water is excessively small, so that when both the acid and base are strongly dissociated, they must be present in very small quantities, and there is practically no hydrolysis. On the other hand, if the salt contains a weak acid or base, having an ionic concentration comparable with that of water, the conditions of equilibrium will require an appreciable amount of acid or alkali, and a considerable fraction of the salt will be found to be hydrolytically dissociated. If the acid is strong and the base weak, there will now be an excess of hydrogen ions, and the solution will have an acid reaction, while if the base is strong and the acid weak, that reaction will be alkaline.

In determining experimentally the amount of hydrolysis in any given case, it is impossible to estimate the acid or base produced by the usual chemical methods, for, by them, the equilibrium would be disturbed, and progressive hydrolysis would eventually decompose all the original salt. Measurements of optical or other physical properties of the solutions can, however, be employed, and the accelerating influence on certain reactions of the free hydrogen or hydroxyl ions has also been used to investigate the subject. The velocity constant for the catalysis of methyl acetate, or the inversion of cane sugar (p. 337), is approximately proportional to the number of free hydrogen ions present in the solution, while the hydroxyl can be estimated by observing the initial rate of saponification of ethyl acetate. The numbers in the first table which follows are given by Walker[1] as the percentage hydrolysis of the hydrochlorides of weak bases, at a temperature of 25°, and a dilution of 32 litres per gram-molecule.

Aniline	2·6	Orthotoluidine	3·1
Paratoluidine	1·5	Urea	76

[1] *Physical Chemistry*, p. 281.

The next table is due to Shields[1], and expresses the percentage hydrolysis of salts of weak acids and strong bases at 24°, and at the given dilutions per gram-molecule.

	Dilution in litres	Hydrolysis
Potassium cyanide	1	0·31
	4	0·72
	10	1·12
	40	2·34
Sodium carbonate	5	2·12
	10	3·17
	20	4·87
	40	7·10
Potassium phenate	10	3·05
	50	6·65
Borax	32	0·92
Sodium acetate	10	0·008

The amount of hydrolytic dissociation being small in all these cases, the mass law simplifies to a proportionality between the percentage ionic concentration and the square root of the dilution (see p. 341), and this result is borne out by the values for the more dilute solutions given above. In all these cases the hydrolysis is slight; but Shields found that trisodium phosphate was about 98 per cent. dissociated into free caustic soda and phosphoric acid at a dilution of 50 litres, and Walker states that salts of the very weak base diphenylamine are almost completely hydrolysed by water.

Another case of considerable hydrolytic dissociation is found in salts of the weak base ferric oxide; in fact, ferric hydrate can be obtained in a soluble form by placing ferric chloride in a vessel separated from a large volume of water by a sheet of parchment paper. After some days, owing to progressive hydrolysis, nearly all the hydrochloric acid will be found to have passed into the water, leaving the iron behind as a brown solution of ferric hydrate.

Since the equivalent conductivity of hydrochloric acid is much greater than that of a normal salt, it is possible to roughly estimate the amount of hydrolysis in a solution of ferric chloride

[1] *Phil. Mag.* (5) xxxv. 365 (1893).

from the conductivity data. Taking the figures for the acid and for the ferric chloride given in the Appendix, and assuming that the equivalent conductivity of a normal salt is about 100 in reciprocal ohms, it is easy to calculate that a solution of ferric chloride at a dilution of 1000 litres is hydrolysed to about 56 per cent. This result neglects the influence of the residual ferric chloride on the dissociation of the acid and is therefore probably too low. Ferric acetate, which has both a weak acid and a weak base, seems to be more completely hydrolysed, the conductivity being of the same order as that of pure acetic acid[1].

Conclusion.

The theory of electrolysis described in this chapter has proved one of the most stimulating hypotheses in the recent history of physical science. At the outset it met with much opposition, chiefly from chemists who held that its fundamental demands were inconsistent with well-established chemical conclusions. At present, criticism comes mainly from another side, and seeks to show that the relations which the theory suggests between the electrical, osmotic, and chemical properties of solutions, aqueous and other, fail when examined experimentally. The reasons for such failure have been pointed out in this chapter; the theory only indicates the relations in question under certain simple conditions, which can seldom be secured in practice. As experimental arrangements approximate to ideal conditions, the correspondence between theory and observation increases, and the variations in other cases are explicable by causes suggested in the development of the theory itself. We must again emphasize the complete mutual independence of the theory of ionic dissociation and any particular view of the nature of solution or the mode of action of osmotic pressure. It is quite possible that solution is a process of chemical combination; the dissociation required by the electrolytic theory is a separation of the opposite ions from each other, and would not in the least prevent a connexion of those ions with molecules of the solvent. Some form of dissociation theory seems to be clearly

[1] Whetham, *Phil. Trans.* A. CLXXXVI. 516 (1895).

indicated by the electrical properties of solutions, and, until these properties are otherwise explained, the theory as at present formulated will be a guide in further investigation. The extended study of more concentrated solutions will throw light on the nature of the interactions between the different solute molecules, and between the solute and the solvent; the effects of these interactions on many of the properties of any given solution are eliminated by working at such extreme dilution that the dissolved substance conforms to the laws of dilute matter. The complete theory of electrolysis needs further experimental data upon which to build, but the fundamental conception of ionic dissociation seems to secure a foundation for further development.

CHAPTER XIII.

DIFFUSION IN SOLUTIONS.

Theory of diffusion. Experiments on diffusion. Diffusion and osmotic pressure. Diffusion of electrolytes. Potential differences between electrolytes. Liquid cells. Complete theory of ionic migration. Electrolytic solution pressure. Diffusion through membranes.

Theory of diffusion.

It is well known that a solution, left to itself, gradually becomes of equal concentration throughout. This process implies an automatic drift of the dissolved substance through the liquid, and has received the name of diffusion.

The diffusion of matter is analogous to the conduction of heat, and Fick[1] applied Fourier's treatment of the latter phenomenon to the elucidation of the former. The quantity of substance which diffuses through unit area in one second may be taken as proportional to the difference in concentration between the fluids at that area and at another parallel area indefinitely near it. This difference in concentration is proportional to the rate of variation of the concentration c with the distance x, so that the number of gram-molecules of solute which, in a time δt, cross an area A of a long cylinder of constant cross section is

$$\delta N_1 = - DA \frac{dc}{dx} \delta t \quad \text{.....(73),}$$

where D is called the diffusion constant or the diffusivity.

[1] *Pogg. Ann.* xciv. 59 (1855).

At another area at a position $x + \delta x$ near the first, the concentration will be $c - \frac{dc}{dx}\delta x$ and the transfer across it is

$$\delta N_2 = -DA\frac{d}{dx}\left(c - \frac{dc}{dx}\delta x\right)\delta t.$$

Hence in unit time the element of volume comprised between the two areas will on the whole gain in contents by

$$\delta N_1 - \delta N_2 = DA\frac{d^2c}{dx^2}\delta x.$$

But the volume of this element is $A\delta x$, and the rate of increase of concentration is dc/dt. We thus obtain the equation of propagation

$$DA\frac{d^2c}{dx^2}\delta x = A\frac{dc}{dt}\delta x,$$

or

$$D\frac{d^2c}{dx^2} = \frac{dc}{dt} \quad \text{.....(74).}$$

This differential equation represents the general nature of diffusion. It can be integrated for definite cases, when the process is simplified by the geometrical and other conditions of the system.

Experiments on diffusion.

A systematic investigation of diffusion without any separating membrane was first made by Graham[1], who immersed in a large volume of water a wide-mouthed bottle containing a solution, and after some time measured the quantity of substance in the water. By this method he found that acids diffused about twice as quickly as neutral salts, and that the rate of diffusion of these salts varied much according to their composition. Two dissolved substances diffused independently of each other, so that it was possible to separate the constituents of some double salts, the alums for example, which are decomposed by water. The quantity which diffused was found to be nearly proportional to the concentration of the original solution, and to depend largely on the temperature. Substances like tannin,

[1] *Phil. Trans.* 1850, pp. 1, 805; 1851, p. 483.

albumen and gums, diffused very much more slowly than the other bodies examined, and only at about one-fiftieth the rate of hydrochloric acid. These less diffusible bodies are non-crystalline, and Graham called them colloids in distinction to the more diffusible crystalloids.

Weber[1] was the first to work out a satisfactory method of determining the absolute value of the diffusion constant in Fick's equation. When two plates of amalgamated zinc are placed in two solutions of zinc sulphate of different concentrations, the solutions being in contact with each other, a difference of electrical potential is produced between the plates which is proportional to the difference in concentration, provided that difference is small. A concentrated solution of zinc sulphate was placed in the lower part of a cylindrical vessel, the bottom of which was made of an amalgamated zinc plate, and a dilute solution gently poured in on the top of the first. The electromotive force between the lower zinc plate and a similar plate placed in the topmost layer of liquid was measured, and found to decrease as the difference in concentration became less. If we apply Fick's law to this case we get an infinite series in the expression for the electromotive force, but when the time is long, the first term only is important, and we get, if H is the height of the vessel, and t the time,

$$E = be^{-\frac{\pi^2}{H^2}Dt} \quad \text{.....(75).}$$

The following table gives the observed values of $\frac{\pi^2}{H^2}D$, which should be constant if Fick's law holds good.

Days	$\frac{\pi^2}{H^2}D$
4—5	·2032
5—6	·2066
6—7	·2045
7—8	·2027
8—9	·2027
9—10	·2049
10—11	·2049
Mean	·2042

[1] *Wied. Ann.* VII. 469 and 536 (1879).

Stefan[1] showed that in the case of a very long cylinder, in which the concentration at one end remains constant, the quantity diffusing through an area A should be, according to Fick's law,

$$N = cA\sqrt{\frac{Dt}{\pi}}.$$

To apply this to a finite cylinder we must imagine that the amount which would have passed beyond the limiting layer is reflected, and, travelling backwards in accordance with the same laws, is added to the quantity present in the lower layers. Experimentally realizing these conditions, Scheffer[2] placed a solution underneath a volume of pure water and measured the quantity of substance which diffused upwards. The following are some of his results, n being the number of molecules of water in which one molecule of substance is dissolved.

Substance	Temperature	n	D
Hydrochloric acid	11	7·2	2·67
" "	11	108·4	1·84
Nitric acid	9	35	1·78
" "	9	426	1·73
Sulphuric acid	8	18·8	1·07
Acetic acid	13·5	84	0·77
Potash	13·6	1665	1·66
Ammonia	4·5	16	1·06
Urea	7·5	110	0·81
Mannite	10	220	0·38

In general the diffusion constant was found to be independent of the dilution, but, in the case of hydrochloric acid, it appeared to increase somewhat with the concentration.

Graham[3] and Voigtländer[4] found that the rate of diffusion in solid agar-agar jelly solutions was nearly the same as in

[1] *Wien. Akad. Ber.* LXXIX. 161 (1879).

[2] *Ber.* XV. 788, XVI. 1903 (1882—3), and *Zeits. phys. Chem.* 390 (1888).

[3] *Phil. Trans.* 1861, p. 183.

[4] *Zeits. phys. Chemie*, III. 316 (1889).

water, and, as these jellies obviate all disturbing effects due to shaking or convection currents, they have been extensively employed. For a 0·72 per cent. solution of sulphuric acid, diffusing into a cylinder of agar jelly, Voigtländer gives the following numbers; N represents the number of milligrams of sulphuric acid diffusing through a given area. The results confirm Stefan's formula.

Time in minutes	N	$N\sqrt{\frac{60}{t}}$
5	0·30	1·04
60	1·08	1·08
480	3·10	1·09
2880	7·05	1·02

The distance to which a determinate concentration reaches is proportional to the square root of the time of diffusion. Thus the formula can be tested and the constants determined by tracing the decolorization of a dilute alkaline solution, coloured red by phenolphthallein, as the acid diffuses upward. The following table, due to Voigtländer, gives the value of the diffusivity at 0°, 20° and 40°, and, in the last two columns, the mean temperature coefficients from 0° to 20° and 20° to 40°.

Substance	D_0	D_{20}	D_{40}	a_1	a_2
Formic acid	0·472	0·867	1·49	·0228	·0306
Acetic „	0·318	0·64	1·04	·0245	·0326
Propionic acid	0·245	0·514	0·882	·0261	·0358
Sulphuric „	0·637	1·21	2·01	·0236	·033
Hydrochloric acid	1·07	2·06	—	·0246	—
Nitric acid	1·10	2·10	—	·0226	—
Potash	1·01	1·75	2·36	·0209	·026
Soda	0·764	1·26	1·35	·0195	·024
Potassium chloride	0·786	1·40	2·18	·0219	·0279
Sodium chloride	0·535	1·04	1·71	·0243	·0332
Calcium „	0·394	—	1·40	—	—
Barium „	0·525	0·98	1·58	·0232	·0306

Diffusion and osmotic pressure.

When the concentration of different parts of a solution is not uniform, the osmotic pressure must also vary. By imagining the parts of the solution separated by ideal semi-permeable membranes, we see that the osmotic pressure is the force per unit area, or the partial pressure, which must be applied, by the diaphragm or otherwise, to the dissolved molecules in bulk in order to prevent their diffusion. By the principle of reaction, it follows that, in a solution of varying concentration, the force which causes diffusive translation of the molecules in a thin slice of the liquid is the reversed difference of osmotic pressures on the two faces of the slice[1]. The phenomena of diffusion have been investigated on these lines by W. Nernst[2] and M. Planck[3]. If we have a vertical cylinder with a solution of some non-electrolyte in its lower part, and pure water at the top, the dissolved substance gradually makes its way upwards through the water, and, neglecting the small disturbing effect of gravity, a uniform solution will finally result. At a height x in the cylinder let the osmotic pressure be P, so that if A be the area of cross section, the substance in the layer whose volume is $A\delta x$ finds itself under the action of a force equal to $-A\delta P$, the negative sign being taken because the force acts in the direction in which the pressure decreases. If c be the concentration in gram-molecules per cubic centimetre, the force which in this layer acts on each gram-molecule is

$$-\frac{A}{cA}\frac{dP}{dx}=-\frac{1}{c}\frac{dP}{dx}.$$

Let F denote the force required to drive one gram-molecule through the solution with the velocity of one centimetre per second. Since the velocity of drift is constant, F must also denote the resistance offered by the viscous medium. The velocity attained is

$$-\frac{1}{cF}\frac{dP}{dx};$$

[1] Larmor, *Aether and Matter*, p. 293.

[2] *Zeits. phys. Chem.* II. 615 (1888); IV. 129 (1889).

[3] *Wied. Ann.* XL. 561 (1890).

and if δN be the number of gram-molecules which cross each layer in a time δt, since the number crossing unit area per second is proportional to the concentration and to the average velocity of the individual molecules, we get

$$\delta N = -\frac{1}{cF}\frac{dP}{dx} Ac\,\delta t = -\frac{1}{F} A \frac{dP}{dx}\delta t.$$

When the solution is dilute, and there is no polymerization or dissociation of molecules with change of concentration, we may apply the gas equation for the osmotic pressure, and write $P = cRT$, the value of the constant R corresponding to one gram-molecule of any substance being taken as usual. This gives

$$\delta N = -\frac{RT}{F} A \frac{dc}{dx}\delta t \quad \text{.....(76).}$$

By comparison with Fick's equation (73)

$$\delta N = -DA\frac{dc}{dx}\partial t,$$

D, the diffusion constant, is seen to correspond to the factor RT/F.

The slow rate of diffusion has led to the adoption of the day instead of the second as the unit of time for experimental work, so that the observed diffusivity D is given by the expression

$$\delta N = -\frac{D}{86400} A \frac{dc}{dx}\delta t.$$

From equation (76) we see that the force required to drive one gram-molecule through the solution with a velocity of one centimetre per second is

$$F = -\frac{RT}{\delta N} A \frac{dc}{dx}\delta t$$

$$= \frac{86400\,RT}{D}.$$

Thus if we know the diffusion constant, we can calculate the force required to produce unit velocity. Voigtländer gives 0·472 as the diffusivity of formic acid at 0° C., and from this we can calculate that the force required to drive one

gram-molecule (46 grams) of formic acid through water with a velocity of one centimetre per second is equal to the weight of 4340 million kilograms. The necessity for such an enormous force is at once realized if we remember the minute size of the molecules and the consequent great influence of the resistance of the medium.

A solution of uniform temperature will in the end become homogeneous; but if the upper layers be kept hotter, the concentration in the lower layers must be greater, in order that the osmotic pressure should be the same throughout. This result was experimentally established by Soret[1] and explained as above by Van 't Hoff[2]. The experiments supply a method of determining the influence of temperature on osmotic pressure, and the results are in accordance with the gas law for dilute solutions.

Diffusion of electrolytes.

If the osmotic pressure-gradient were the only driving force, the different mobility of the two ions of an electrolyte, such as hydrochloric acid, would cause separation between them.

In a solution of hydrochloric acid at the bottom of a tall glass cylinder, with pure water lying above it, the hydrogen ions travel faster than the chlorine, and carry their positive charges with them, leaving the lower layers negatively charged. An electrostatic force thus arises, which opposes the process of separation, and keeps the number of opposite ions in each part of the system very nearly the same. Nevertheless some separation does occur, and this explains the fact that water, in contact with an aqueous solution of an electrolyte, takes, with regard to it, a positive or negative potential as the positive or negative ion travels the faster.

When solutions of two different electrolytes are placed in contact, a similar state arises. Let us suppose that we have a solution of hydrochloric acid in contact with one of lithium bromide. On the one hand more hydrogen ions than chlorine ions will diffuse out of the acid solution, and therefore the

[1] *Ann. Chim. Phys.* xxii. 293 (1881).
[2] *Zeits. phys. Chem.* i. 487 (1887).

salt solution will receive a positive charge. On the other hand, more bromine ions than lithium ions will diffuse from the salt solution into the acid, and thus the potential difference will be increased.

Let us return to the consideration of the solution of a single electrolyte containing two monovalent ions, placed beneath pure water. From the velocities of the two ions under unit potential gradient, as found by Kohlrausch's theory, it is easy to deduce the velocity with which they will travel when unit force acts on them. Let us call these velocities U and V for the cation and anion respectively. The actual velocities in our case will therefore be $-\frac{U}{c}\frac{dP}{dx}$ and $-\frac{V}{c}\frac{dP}{dx}$, so that the amounts passing any cross section of the cylinder in a time δt are

$$-UA\frac{dP}{dx}\delta t \text{ and } -VA\frac{dP}{dx}\delta t.$$

When U is different from V, a difference of potential is set up; with the effect, on reaching a steady state of electric separation, of making the ions travel together. If the potential gradient is dE/dx the force on a gram-equivalent of an ion carrying a charge q is qdE/dx, and numbers of the two ions which would cross, under the action of this force alone, are

$$-UAcq\frac{dE}{dx}\delta t \text{ and } +VAcq\frac{dE}{dx}\delta t.$$

Under the influence of both the osmotic and the electric forces the number of gram-equivalents which diffuse in a given time must be equal, so that we get

$$\delta N = -UA\delta t\left(\frac{dP}{dx}+cq\frac{dE}{dx}\right) = -VA\delta t\left(\frac{dP}{dx}-cq\frac{dE}{dx}\right);$$

or eliminating dE/dx,

$$\delta N = -\frac{2UV}{U+V}A\frac{dP}{dx}\delta t.$$

For dilute solutions we may assume that the gaseous laws hold good, so that

$$P = cRT,$$

c, the concentration, being the reciprocal of the volume in which one gram-molecule is dissolved.

Therefore $$\delta N = -\frac{2UV}{U+V} RTA \frac{dc}{dx} \delta t.$$

We shall need the intermediate steps of this investigation when we consider Nernst's account of contact differences of potential; this last equation merely states that the resistance offered by the liquid to the passage of an electrolyte is the sum of the resistances offered to the passage of its ions, and can be directly deduced on that assumption without further electric hypotheses. Thus the osmotic pressure of a binary electrolyte has double the normal value, so that the number of gram-molecules of hydrochloric acid diffusing across any section of the vessel in a time δt is, by equation (76),

$$\delta N = -\frac{2RT}{F} A \frac{dc}{dx} \delta t.$$

The resistances to hydrogen and chlorine moving with unit velocity are $1/U$ and $1/V$ respectively, so that the resistance to hydrochloric acid is

$$F = \frac{1}{U} + \frac{1}{V} = \frac{U+V}{UV},$$

and we recover Nernst's equation

$$\delta N = -\frac{2UV}{U+V} RTA \frac{dc}{dx} \delta t.$$

From the general theory of diffusion we have already deduced equation (73)

$$\delta N = -DA \frac{dc}{dx} \delta t.$$

By comparing this with Nernst's equation, we see that, for electrolytes, the diffusion constant is given by the expression

$$D = \frac{2UV}{U+V} RT.$$

T is the absolute temperature, R the gas constant corresponding to one gram-equivalent of substance, 1·980 calories per degree or $8{\cdot}284 \times 10^7$ ergs per degree, so that it only remains to calculate U and V, the velocities with which the ions move

under the action of unit force. The quantity of electricity associated with one gram-equivalent of any ion is ± 9644 electromagnetic units. If the potential gradient is one volt (10^8 C.G.S. units) per centimetre, the force acting on this gram-equivalent will be 9644×10^8 dynes. This, in dilute solution, gives the ion its specific velocity, say u. Thus the force P_W required to give the ion unit velocity is $9{\cdot}644 \times 10^{11}/u$ dynes or $9{\cdot}83 \times 10^5/u$ kilograms weight. If the ion have an equivalent weight W, the force P_1 producing unit velocity when acting on one gram is $9{\cdot}83 \times 10^5/Wu$ kilograms weight. Thus, in order to drive one gram of potassium ions with a velocity of one centimetre per second through a very dilute water solution, a force is required equal to the weight of 38,000,000 kilograms. The table gives other examples[1].

	Kilograms weight			Kilograms weight	
	P_W	P_1		P_W	P_1
K	15×10^8	38×10^6	Cl	14×10^8	40×10^6
Na	22 „	95 „	I	14 „	11 „
Li	27 „	390 „	NO_3	15 „	25 „
NH_4	15 „	83 „	OH	5·4 „	32 „
H	3·1 „	310 „	$C_2H_3O_2$	27 „	46 „
Ag	17 „	16 „	$C_3H_5O_2$	30 „	41 „

Since the ions move with uniform velocity, the frictional forces brought into play must be equal and opposite to the driving forces acting, and therefore these numbers also represent the ionic friction coefficients in very dilute solution at 18° C.

Let us now return to the consideration of the velocity. We have seen that the force acting on one gram-equivalent of an ion, when the potential gradient is one volt per centimetre, is 9644×10^8 dynes, and that, in dilute solution, this gives to the ion its specific velocity u. The velocity it would attain under unit force will therefore be

$$U = \frac{u}{9644} \times 10^{-8} \text{ cms. per second.}$$

[1] Kohlrausch, *Wied. Ann.* L. 385 (1893).

In the case of hydrochloric acid, for example, the specific mobility of the hydrogen is 0·0032, and that of the chlorine 0·00069; thus

$$U = 3{\cdot}32 \times 10^{-15}, \text{ and } V = 7{\cdot}15 \times 10^{-16}$$

and, for the diffusion coefficient, we have

$$D = \frac{2UV}{U+V} RT = 2{\cdot}49,$$

the velocities, for convenience, being reckoned in centimetres per day.

The agreement between theory and Scheffer's observations on diffusion is shown by the table.

Substance	*D* observed	*D* calculated
Hydrochloric acid, HCl	2·30	2·49
Nitric acid, HNO_3	2·22	2·27
Potash, KOH	1·85	2·10
Soda, NaOH	1·40	1·45
Sodium chloride, NaCl	1·11	1·12
Sodium nitrate, $NaNO_3$	1·03	1·06
Sodium formate, NaCOOH	0·95	0·95
Sodium acetate, $NaCO_2CH_3$	0·78	0·79
Ammonium chloride, NH_4Cl	1·33	1·44
Potassium nitrate, KNO_3	1·30	1·38

The theoretical numbers are slightly increased by the assumption that the ionization of the solutions is complete, which is not accurately the case. This correction, then, would improve the agreement. The possibility of thus correctly calculating the diffusion constant must be regarded as very strong evidence in favour of the methods of the investigation.

Further developments for the cases of other solvents and of mixed electrolytes have been traced by Arrhenius[1], who shows, for example, that the rate at which hydrochloric acid diffuses will be increased by the presence of one of its salts. This is confirmed experimentally; when 1·04 normal HCl diffuses into 0·1 NaCl, *D* is calculated as 2·43 and observed as 2·50, and when the NaCl solution is 0·67 normal, calculation gives 3·58 and observation 3·51.

[1] *Zeits. phys. Chem.* x. 51 (1892).

Potential differences between electrolytes.

As we have seen above, when a solution is placed in contact with water, the water, which becomes a dilute solution, will take a positive or negative potential with regard to the stronger solution, in accordance with the greater specific mobility of the cation or the anion. Taking the equation which expresses the relation that, when a steady state is reached, the ions migrate at equal rates, viz.

$$UA\delta t\left(\frac{dP}{dx}+cq\frac{dE}{dx}\right)=VA\delta t\left(\frac{dP}{dx}-cq\frac{dE}{dx}\right),$$

we get

$$\frac{dE}{dx}=\frac{1}{cq}\frac{V-U}{V+U}\frac{dP}{dx};$$

or, since for dilute solutions $P=cRT$,

$$\frac{dE}{dx}=\frac{RT}{Pq}\frac{V-U}{V+U}\frac{dP}{dx},$$

which gives on integration

$$E=\frac{RT}{q}\frac{V-U}{V+U}\log_e\frac{P_2}{P_1},$$

where P_1 and P_2 denote the osmotic pressures of the ions in the dilute and concentrated solutions respectively, and E denotes the difference of potential, i.e. the electromotive force between the two liquids. Now U and V, the ionic velocities under unit forces can, by multiplying by q, the quantity of electricity associated with one gram-equivalent of an electrolyte, be transformed into u and v, the velocities under unit potential gradient. We have already restricted the investigation to the case of dilute solutions, so that we can also replace the ratio between the two osmotic pressures by the corresponding ratio between the two concentrations. The equation now becomes

$$E=\frac{RT}{q}\frac{v-u}{v+u}\log\frac{c_2}{c_1} \quad \text{.....(77).}$$

Thus the potential difference between two solutions with different concentrations of the same electrolyte, containing only univalent ions, is proportional to $v-u$, the difference between the mobilities of the anion and the cation.

If the valency of the cation be y_1 and that of the anion y_2, a similar investigation shows that

$$E = \frac{RT}{q} \frac{\frac{v}{y_2} - \frac{u}{y_1}}{v+u} \log \frac{c_2}{c_1} \quad \text{.....(78).}$$

Liquid cells.

In order to compare these equations with observation, Nernst[1] devised a form of concentration cell in which the electromotive force depends only on the two solutions. Such arrangements are sometimes known as liquid cells. We may take as an example, the following series:

Hg/HgCl/0·1 normal
KCl/0·01 KCl/0·01 HCl/0·1 HCl/0·1 KCl/HgCl/Hg.

Two things are here to be observed; the first, that the ends of the chain are identical, and the potential differences there neutralize each other; the second, that, in dilute solutions, it is only the ratio and not the absolute values of the osmotic pressures or the concentrations that are involved. Thus the effect at the junction 0·01 KCl/0·01 HCl is equal and opposite to that at the junction 0·1 HCl/0·1 KCl, and the only effective junctions are those between 0·1 KCl/0·01 KCl and between 0·01 HCl/0·1 HCl. From the ionic mobilities of potassium, chlorine and hydrogen, the difference of potential at each of these junctions can be calculated, and the sum of the two results compared with the experimental value of the electromotive force of the arrangement. The following table gives the results of Nernst's comparison of the calculated and observed values for this and other similar liquid cells.

Electrolytes	E.M.F. calculated	E.M.F. observed
KCl, NaCl	0·0132	0·0111
KCl, LiCl	0·0203	0·0183
KCl, NH_4Cl	0·0010	0·0004
NH_4Cl, NaCl	0·0122	0·0098
KCl, HCl	−0·0383	−0·0357
KCl, HNO_3	−0·0400	−0·0378
KCl, $C_9H_{11}SO_3H$	−0·0502	−0·0469

[1] *Zeits. phys. Chem.* IV. 129 (1889).

The more general case of any two electrolytes in contact with each other has been considered by Planck[1]. The equations are somewhat complicated, but, when the total concentration of the ions in the two solutions is the same, and all the ions have the same valency y, the expressions reduce to the simple form,

$$E = \frac{RT}{qy} \log \frac{u_1 + v_2}{u_2 + v_1}.$$

Nernst has determined the electromotive force of cells which can be used to verify this equation; the following are the results of the comparison.

Electrolytes	E (calculated)	E (observed)
HCl, KCl	0·0282	0·0285
HCl, NaCl	0·0334	0·0350
HCl, LiCl	0·0358	0·0400
KCl, NaCl	0·0052	0·0040
KCl, LiCl	0·0077	0·0069
NaCl, LiCl	0·0024	0·0027

Complete theory of ionic migration.

Hittorf's account of the phenomena of ionic migration deals only with the initial changes of concentration which appear at the two electrodes on the passage of a current, before the diffusion that supervenes produces a sensible effect[2]. As long as the middle part of the solution retains its original concentration, Hittorf's investigation holds good, and this condition must be maintained in experimental measurements of transport numbers.

When the current flows for a long time, the electrode regions of densities modified by the current extend and meet each other, and the results of backward diffusion become important. The general problem of electrolytic conduction which then arises has been investigated by the use of Fourier's

[1] *Wied. Ann.* XXXIX. 161; XL. 561 (1890); account in Ostwald's *Lehrbuch*, II. 848.

[2] See above, pp. 208—212.

diffusion analysis by Planck, Larmor[1], and others, on the assumptions that the ions both migrate and diffuse independently of each other and that the ionization is complete. Ultimately a steady state will be reached; with a constant current and a non-dissolvable anode, the concentration diminishes uniformly with the time as the electrolysis proceeds, and its gradient has a definite value irrespective of the value of the concentration itself, changing uniformly from $I/2RTqu$ at the anode to $-I/2RTqv$ at the cathode, where I denotes the current, R the usual gas constant per gram-molecule, T the absolute temperature, q the electric charge on one gram-equivalent of a monovalent ion, u the mobility of the cation, and v the mobility of the anion. The difference in the concentrations at the anode and cathode in the steady state is found to be

$$\frac{Il}{2qD}\frac{u-v}{u+v},$$

which is equal to Hittorf's difference produced initially per unit time divided by D/l, D being the diffusion constant and l the length between the electrodes. As the ions diffuse at different speeds, whether electrolysis is going on or not, any changes of concentration at once give rise to internal electromotive forces. Even when the steady state is reached, the gradient of electromotive force is of complex character. When the applied electromotive force is kept constant, and the current allowed to change, the quantities will vary exponentially with the time.

A special case of Larmor's equations, in which the circuit is imagined to be broken, so that the current is zero, gives Nernst's expressions for the potential differences at the interface of two solutions of an electrolyte of different concentrations. Here the state of concentration is not steady, the only possible steady state being one of uniform density.

Another application of the principles of the investigation enables the effect of a transverse magnetic field to be examined, and the coefficient of the resultant Hall effect to be calculated; for, by the laws of electrodynamics, a transverse magnetic field

[1] *Aether and Matter*, p. 291.

must produce a sideways force on the moving ions which constitute the current. Larmor shows[1] that a magnetic field H is equivalent to a transverse uniform electric force F which, if c denotes the concentration of the solution, has the value

$$F = \frac{v-u}{v+u}\frac{IH}{2cq}.$$

An investigation of the more general case which arises when the electrolyte is only partially ionized, has been given by F. G. Donnan[2].

Electrolytic solution pressure.

Nernst's hypothesis of a solution pressure of metals in contact with electrolytic solvents may also be approached from the point of view of ionic diffusion. To each metal is ascribed a definite solution pressure, depending only on the nature of the solvent and the temperature; this pressure tends to carry the metal into solution in the form of positively charged ions. The process will electrify the solution positively, and leave the metal with a negative charge. In this manner, according to Nernst, is set up the potential difference at the surface of the metal, the phenomena of which we have previously studied. The electric forces will oppose the further solution of the metal, tending to drive back again the ions already in the liquid. The electrostatic charges on the ions are very great, and the potential difference of equilibrium may be reached long before a weighable quantity of metal has been dissolved.

On any view, the process of solution can only continue if negative ions can simultaneously dissolve, or other positive ions be removed from solution. The latter condition is illustrated by the replacement of hydrogen in acids, or the precipitation of one metal by another. When hydrogen is evolved, it is probable that it is first dissolved by the metal, from which it separates when its vapour pressure exceeds that of the atmosphere. The action can be stopped by a sufficient external

[1] *Phil. Trans.* CLXXXV. A. 815 (1894), or *loc. cit.*

[2] *Phil. Mag.* Nov. 1898.

pressure, the value of which can be determined by thermodynamic considerations, and, on Nernst's ideas, depends on the solution pressure of the metal. Thus Beketoff[1] and Brunner[2] have shown that hydrogen at a high pressure can precipitate silver, platinum and palladium; Cailletet arrested its evolution from zinc and sulphuric acid; while Nernst[3] and Tammann[4] have examined the action of other metals.

From Nernst's standpoint, this process of metallic solution is analogous to the diffusion of ions across the interface between a concentrated and a dilute solution of the same electrolyte. Such a metal as zinc is looked on as a solvent in which the concentration and the osmotic pressure of its own positive ions are very high. Some of these ions diffuse into a liquid in contact with the metal, till the characteristic ionic potential difference is set up. The electric forces then prevent further change, and, since the metal maintains the constancy of its ionic concentration, the osmotic pressures on the two sides of the interface are never equalized, unless the metal and solvent happen to show no difference of potential.

We have seen that on Nernst's theory of electrolytic diffusion, the potential difference between two solutions of an electrolyte of different concentrations can be expressed as

$$E = \frac{RT}{q} \frac{v-u}{v+u} \log \frac{P_2}{P_1}.$$

If, ignoring the essential difference in the two cases, we extend this equation to the interface between a metal m and a solution, we are concerned with the cation only, for no anion is transferred across the boundary. Thus v is zero and we get

$$E = -\frac{RT}{q} \log \frac{P_m}{P_1}$$

where P_m now denotes the osmotic pressure of the cations in the substance of the metal itself, that is, its solution pressure. We thus regain the equation which was deduced in a former

[1] *Compt. Rend.* XLVIII. 422 (1889).
[2] *Pogg. Ann.* CXXII. 153 (1864).
[3] *Compt. Rend.* LXVIII. 395 (1869).
[4] *Zeits. Phys. Chem.* IX. 1 (1892).

chapter (p. 257) from a consideration of the osmotic work equivalent to unit electric transfer. We have already considered the limitations of this equation and pointed out that, following Helmholtz, the term involving P_m may be treated as an affinity constant, characteristic of the metal and the solvent.

In applying these considerations to common chemical galvanic cells, such as Daniell's, we neglected the electromotive force at the junction of the liquids; as will now be clear, the theory of ionic diffusion enables us, in simple cases, to supply the term previously missing from the equation.

In concentration cells the metal is the same at each electrode, so that P_m can be eliminated; it is therefore possible to develop the theory of such cells from the study of ionic diffusion. For a monovalent metal, such as silver, we have

$$E = \frac{RT}{q}\left(\log\frac{P_{Ag}}{P_1} - \frac{v-u}{v+u}\log\frac{P_1}{P_2} - \log\frac{P_{Ag}}{P_1}\right)$$

$$= \frac{RT}{q}\,\frac{2v}{u+v}\log\frac{P_2}{P_1}.$$

Since $v/(u+v)$ is for dilute solutions equal to r, the transport ratio for the anion, and n, the number of ions given by a molecule of the electrolyte, is here 2, this result is identical with equation (50) on p. 248. By similar methods we can regain the equations already given in Chapter X. for other kinds of concentration cell.

The exact significance of the physical constant named 'solution pressure' is uncertain. Following Nernst, Ostwald considers that, in a given solvent, it is a function of the metal and temperature only, and consequently that the single potential difference at the interface is independent of the nature of the negative ion. Measurements, in part described in Chapter XI., of the potential differences at single reversible junctions, when the cation is of the same metal as the electrode, have often been made from this point of view. We may here again refer to those of Le Blanc[1] and Neumann[2]. These observers measured the electromotive forces of cells made up

[1] *Zeits. phys. Chem.* XII. 345 (1893).

[2] *Zeits. phys. Chem.* XIV. 225 (1894).

with the junction in question at one electrode, and mercury in the usual normal potassium chloride solution with an excess of calomel at the other. Assuming the potential difference between the electrolytes to be small, Neumann found that at great dilution the electromotive force of the cell was in general independent of the anion; but Paschen, Bancroft, and other observers, working with metals in solutions not of their own salts (arrangements which possibly form limiting cases of reversible electrodes and are subject to the same laws), have found that the potential difference does depend on the anion when the metal is copper, platinum, or mercury. Many experiments on cells containing non-reversible electrodes have been made to determine the influence of the nature of the ions and of concentration. Among these experiments we may mention those of Paschen[1], Ostwald[2], Oberbeck and Edler[3], Bancroft[4], and A. E. Taylor[5]. Taylor suggests that the differences found by some of the observers on changing the anion may be due to large potential differences of non-osmotic type at the surface of contact of the two liquids in the cells, for he finds that such large differences often arise in cases where there is a tendency to form complex salts.

Diffusion through membranes.

Before Graham's experiments on free diffusion through water, many observations had been made on the passage of dissolved matter through various animal and vegetable membranes. Such membranes, made of bladder, parchment paper, and similar materials, are of the nature of colloids, and appear to be quite impermeable to other colloidal substances. Solutions of colloids may be freed from crystalloids by placing the mixture in a vessel closed by a membrane, which, on its other side, is in contact with a large volume of the pure solvent. The crystalloids pass through, and, after a considerable time, are completely separated from the dissolved colloids. The process is known as dialysis.

[1] *Wied. Ann.* XLIII. 590 (1891).

[2] *Zeits. phys. Chem.* I. 583 (1887).

[3] *Wied. Ann.* XLII. 209 (1891).

[4] *Zeits. phys. Chem.* XII. 289 (1893); *Physical Review*, III. 250 (1896).

[5] *Jour. Phys. Chem.* I. 1 and 81 (1896).

The rate at which crystalloids pass through one of these membranes depends on the nature both of the diffusing substance and of the membrane. Water will usually pass more freely than salts dissolved in it, and thus a temporary osmotic pressure can be obtained by using a membrane of bladder or parchment paper. The septum is not a perfect semi-permeable wall, however, and the limiting value of the osmotic pressure is never reached; gradually the salt diffuses outwards, and the concentration of the liquid becomes identical on both sides. The relative rates of passage of solute and solvent were shown by Eckard[1] to depend on the nature of the membrane, which must therefore also control the temporary pressure observed. The true maximum value of the osmotic pressure, which we have studied in Chapter V., can only be obtained by aid of a perfect semi-permeable wall, and must clearly be independent of the nature of the partition; for if not, a perpetual motion arrangement could at once be devised. With the membranes we are now considering, irreversible processes are involved, and the conditions are entirely different from those which theoretically hold when an ideal perfect semi-permeable wall is used. Such ideal partitions are theoretically possible, and, by making use of this idea, we can simplify the application of the principles of thermodynamics to the elucidation of the phenomena of solution. It is however very difficult to construct perfect semipermeable membranes, and a considerable number of those prepared in accordance with the directions given on p. 96 will always be found to show some leakage of salt. The greatest pressure actually reached will then vary with different membranes, but this variation is a consequence of the imperfection of the partition, which allows some of the available energy of mixture to pass directly into heat, and, in accordance with theory, vanishes if membranes are obtained which show no leakage. The theories which we have developed cannot be applied to the phenomena shown by leaking membranes, whether natural or artificial, for such leakage must render the system essentially irreversible. Nevertheless, the study

[1] *Pogg. Ann.* CXXVIII. 61 (1866).

of the temporary pressures which can be obtained by the help of organic membranes, the rate of diffusion of different substances through them, and their thermodynamic or osmotic efficiency, are problems of fundamental importance for the physiologist.

The mode of action of the membrane is at present little understood. The various possible views are described on p. 97, under the head of inorganic semi-permeable membranes, and it is as yet impossible to say if the separating process depends (1) on a mechanical sieve-like action, (2) on the saturation of the membrane or the formation of loose chemical compounds with it on one side and their decomposition on the other, or (3) on the filtering action of capillarity explained on p. 98. As there suggested, it is possible that the three modes of explanation may run into each other, different aspects being more prominent in different cases.

CHAPTER XIV.

SOLUTIONS OF COLLOIDS.

The colloidal state. Process of gelation and structure of gels. Coagulative power of electrolytes. The nature of colloidal solutions.

The colloidal state.

THERE is a marked difference in physical and chemical properties between bodies of definite crystalline form, such as most inorganic salts and minerals, and soft or amorphous substances, such as albumen and the various kinds of jelly. Graham distinguished the two groups as crystalloids and colloids respectively, and particularly examined them with regard to their relative diffusive powers. Many different kinds of chemical compounds show colloidal properties. Besides a vast number of animal and vegetable substances, some of which seem to play a great part in the phenomena distinctive of living matter, many of the precipitates which are formed in the course of inorganic chemical reactions appear in an amorphous or colloidal state. The sulphides of slightly oxidizable metals such as antimony and arsenic are good examples. Thus if a solution of arsenious acid is allowed to flow into water saturated with sulphuretted hydrogen by means of a continuous current of the gas, a colloidal hydrosulphide is formed, which can be freed from excess of sulphuretted hydrogen by passing a current of hydrogen, and from salts by dialysis. Many hydrates, too, are colloids, ferric hydrate, for instance, which can readily be prepared from the corresponding salts of iron. By treating dilute solutions of gold chloride with

reducing agents, such as a few drops of a solution of phosphorus in ether, the gold is set free in the colloidal condition, forming a ruby-coloured solution which can be purified by dialysis. Silver, bismuth and mercury can also be obtained in colloidal solution. Colloid solutions seem to be non-conductors of electricity, the dissolved colloids moving as a whole up or down the potential gradient in the same way as non-conducting solid particles.

The classification of substances into colloids and crystalloids again brings us to the study of that part of our subject which is concerned with the phenomena of allotropy, amorphous modifications, and crystallization, and has been referred to on pp. 45 to 47 in the chapter on the Phase Rule. If, as there indicated, a true solid is always crystalline, colloids which possess some of the properties of solids must really be undercooled liquids; in fact, such a view of their nature was suggested by Graham[1]. Fluid colloids seem to be capable of existing in a coagulated or insoluble condition, which they readily assume under a slight disturbing influence. The solution of hydrated silica, for instance, may remain liquid for days or weeks in a sealed tube, but is sure to coagulate at last. The existence in nature of mineral and crystalline forms of silica, which have been deposited from water, suggests that, even in its coagulated condition, the colloidal substance is unstable, passing eventually into a crystalline variety. Glass, too, usually a typical colloid, may become crystalline with lapse of time. We may conclude, then, that colloids are essentially unstable bodies, never in true equilibrium, though the forces, viscous or other, opposing a change of state, may be so large that the condition will persist for a very long time.

When examined chemically, colloids show very little activity, and chemical changes are produced in them slowly and with difficulty. They freely form addition products, however, with such bodies as water and alcohol, such combined water or alcohol being readily interchangeable with other similar substances. The process of absorption of water is often accompanied

[1] *Phil. Trans.* CLI. 183 (1861); Collected Papers, p. 553.

with considerable increase of volume. The corresponding contraction when the water is removed by evaporation sometimes gives rise to considerable forces; a solution of isinglass, drying in a glass vessel over sulphuric acid *in vacuo*, may tear away strips from the surface of the glass owing to its strength of adhesion. Many solid colloids, and solid solutions of colloids and water, can be used as solvents for mineral salts and acids; as we have stated (pp. 217, 372), the ionic mobility and the diffusivity are then very little less than in liquid aqueous solutions of equivalent strength. On the other hand, the power of separating colloids and crystalloids by dialysis shows that colloidal membranes are almost impermeable to other colloids.

Solutions of colloids in crystalloid solvents, such as water or alcohol, seem to be divisible into two classes. Both classes appear to mix with warm water in all proportions, and the mixture will solidify under certain conditions to form a mass which may be called a gel; but one class, represented by gelatine and agar jelly, will, when solidified, redissolve on warming or dilution, while the other class, containing such substances as hydrated silica, albumen, and metallic hydrosulphides, will, under the influence of heat or on the addition of electrolytes, form gels which cannot be redissolved. The solidification of members of the first class into redissolvable substances is termed setting, that of substances in the second class, which form insoluble precipitates, is termed coagulation[1]. Liquid solutions of colloids in water have been called by Graham hydrosols, and the solids, formed by setting or coagulation, hydrogels. Hardy has distinguished the two kinds of systems forming soluble and insoluble precipitates as reversible and non-reversible[2]. The names are convenient, but as there appears to be a considerable difference between the melting and solidifying points of jellies, etc., it must be understood that such systems are not necessarily reversible in the thermodynamic sense of the word.

[1] W. B. Hardy, *Proc. R. S.* LXVI. 95 (1900).
[2] *loc. cit.*

Process of gelation and structure of gels.

The mechanism of gelation in reversible colloidal systems has been studied experimentally by van Bemmelen[1] and by Hardy.

Van Bemmelen measured the vapour pressures of gels which had been formed by the coagulation of hydrated silica and contained varying proportions of absorbed water. When water is removed slowly, a regular continuous curve is obtained; when the removal is rapid, the diagram shows changes of curvature. Van Bemmelen considers that the system does not consist of two definite phases in the sense of the Phase Rule, for the two parts into which it separates on coagulation are not divided by a definite interface. Still, two parts can be distinguished, one of which is colloidal, viscous, and possesses a net-like structure in which the other more fluid liquid is partly absorbed and partly retained mechanically. The colloidal liquid passes into the solid state by the lapse of time or by the influence of foreign bodies.

The emission and absorption of water vapour by colloidal matter has been investigated theoretically by Duhem[2], who deduces the results observed by van Bemmelen from the thermodynamic properties of a system of which two of the controlling variables are subject to hysteresis.

Hardy examined mixtures of agar and water, agar water and alcohol, and gelatine water and alcohol. The last-named ternary system gives a homogeneous liquid when warm, but divides on cooling into two phases possessing different refractive indices, and is therefore suitable for microscopic investigation. When the proportion of gelatine is small, from 6 to 14 per cent., fluid droplets are seen to form as the liquid cools; they solidify and eventually join together into a loose framework. The mass has then become a more or less solid gel. With a higher proportion of gelatine, 36·5 per cent., this arrangement was inverted, and the drops formed contained less gelatine than the residual substance, which now forms a solid solution, interrupted by spherical spaces filled with liquid. The temperature at which the separation into two phases occurs is raised by an

[1] *Zeits. anorgan. Chem.* XIII. 233 (1896); XVIII. 14 (1898).

[2] *Jour. Phys. Chem.* IV. 65 (1900).

increase in the proportions of gelatine or alcohol, and lowered by the addition of the common solvent water. No binary system was found in which the changes could be followed by the microscope; but with a mixture of agar and water, the gel could be separated into two phases consisting of a solid and a liquid solution respectively, by expressing the latter through canvas. The constitution is therefore probably similar to that investigated for the three-component system described above.

Coagulative power of electrolytes.

Graham observed that the addition of salts, sometimes in minute quantities, often caused colloidal solutions to coagulate[1]. Hydrated alumina, for instance, prepared by dialysing a solution of the chloride containing excess of the hydrate, was so unstable that a few drops of well-water at once produced coagulation, and the same change was brought about by pouring the solution into a new glass vessel, unless the vessel had repeatedly been washed with distilled water. This action of salts was further investigated by Schulze[2], who found that hydrosols of sulphide of arsenic were coagulated by salts at a rate depending largely on the valency of the metal. Defining the coagulative power as the reciprocal of the concentration in gram-molecules per litre necessary to coagulate a given solution, Schulze found that the relative coagulative powers of univalent, divalent, and trivalent metals were in the ratios 1 : 30 : 1650. These results were verified by Prost[3], who used sulphide of cadmium as the colloid, and by Linder and Picton[4], working with sulphide of antimony. Linder and Picton found that a slight trace of the metal is entangled in the coagulum, the salt apparently being decomposed to a corresponding extent. Their measurements showed that, for different salts of a given metal, the coagulative powers are proportional to the equivalent electrical conductivities, and that the relative coagulative powers of various

[1] Collected Papers, p. 580.
[2] *Jour. prakt. Chem.* xxv. 431 (1882).
[3] *Bull. Acad. Roy. Sci. de Belg.* [3] xiv. 312 (1887).
[4] *Jour. Chem. Soc. Trans.* lxvii. 63 (1895).

sulphates of univalent, divalent, and trivalent metals ranged round the mean values 1 : 35 : 1023. The effect of adding a small quantity of the salt of one metal was to reduce the amount of the salt of another metal with the same valency which was required for coagulation; but if the metal of the second salt had a different valency, the amount of salt needed was actually increased by the presence of the first salt: more strontium chloride, for instance, was necessary when a little potassium chloride was previously dissolved. It is probable that the molecular changes which accompany coagulation are not sudden discontinuous processes, for Linder and Picton[1] found that, as the point of coagulation is approached, the size of the colloid particles increases even though actual coagulation does not occur, and, under similar conditions, Graham[2] observed a gradual increase in the viscosity of the solution.

An explanation of some of these remarkable valency relations has been offered by the present writer[3]. The connexion with electrical conductivity discovered by Linder and Picton shows that the coagulative power of a salt depends on its electrical properties. Let us suppose that, in order to produce the aggregation of colloidal particles which constitutes coagulation, a certain minimum electrostatic charge has to be brought within reach of a colloidal group, and that such conjunctions must occur with a certain minimum frequency throughout the solution. Since the electrical charge on an ion is proportional to its valency, we shall get equal charges by the conjunction of $2n$ triads, $3n$ diads, or $6n$ monads, where n is any whole number.

In a solution where ions are moving freely, the probability that an ion is at any instant within reach of a fixed point is, putting certainty equal to unity, approximately represented by a fraction proportional to the ratio between the volume occupied by the spheres of influence of the ions and the whole volume of the solution, and may be written as Ac, where A is a constant

[1] *Jour. Chem. Soc. Trans.* LXVIII. 73 (1895).

[2] Collected Papers, p. 619.

[3] *Phil. Mag.* [5] XLVIII. 474 (1899); also Hardy and Whetham, *Jour. Physiology*, XXIV. 288 (1899).

and c represents the concentration of the solution. The chance that two such ions should be present together is the product of their separate chances, that is, $(Ac)^2$. Similarly, the chance for the conjunction of three ions is $(Ac)^3$, and for the conjunction of n ions is $(Ac)^n$.

In order that three solutions, containing trivalent, divalent, and univalent ions respectively, should have equal coagulative powers, the frequency with which the necessary conjunctions should occur must be the same in each solution. We should then have, the constant being assumed equal in each case,

$$A^{2n}c_3^{2n} = A^{3n}c_2^{3n} = A^{6n}c_1^{6n} = \text{a constant} = B.$$

Therefore

$$c_3 = \frac{B^{\frac{1}{2n}}}{A}, \quad c_2 = \frac{B^{\frac{1}{3n}}}{A}, \quad c_1 = \frac{B^{\frac{1}{6n}}}{A},$$

c_1, c_2, c_3 representing the concentrations of monads, diads, and triads in their respective solutions. Thus we get for the ratios of the concentrations of equi-coagulative solutions

$$c_1 : c_2 : c_3 = B^{\frac{1}{6n}} : B^{\frac{1}{3n}} : B^{\frac{1}{2n}} = 1 : B^{\frac{1}{6n}} : B^{\frac{1}{3n}}.$$

Let us put $B^{\frac{1}{6n}} = \frac{1}{x}$; the ratios can then be written

$$1 : \frac{1}{x} : \frac{1}{x^2}.$$

The reciprocals of the numbers expressing the relative concentrations of equi-coagulative solutions give values proportional to the coagulative powers of solutions of equal concentration; so that, calling the coagulative powers of equivalent solutions containing monovalent, divalent, and trivalent ions respectively p_1, p_2, p_3, we get

$$p_1 : p_2 : p_3 = 1 : x : x^2.$$

Let us now take some numerical examples. Putting $x = 32$, we get the series

$$1 : 32 : 1024,$$

which agrees very well with Linder and Picton's results for colloidal solutions of antimony sulphide,

$$1 : 35 : 1023;$$

and putting $x = 40$, we get

$$1 : 40 : 1600,$$

numbers comparable to Schulze's values for sulphide of arsenic,

$$1 : 30 : 1650.$$

When we consider the difficulty of the experiments, and remember that the coagulative powers of solutions containing different ions of equal valency are not equal, but vary as the equivalent conductivities, these results show a better agreement between the calculated and observed values than might have been expected.

The particles in solutions of colloids in water generally move when in an electric field, the direction of motion depending on the nature of the colloid and of the solvent. Thus Hardy[1] found that proteid, modified by heating to the boiling point when dissolved in water, reverses the direction of its motion under the influence of electric forces, when the reaction of the fluid holding it is changed from slightly acid to slightly alkaline. A minute quantity of free alkali causes the proteid particles to move against the current, while the addition of an equally minute quantity of acid is followed by movement in the same direction as the current. Movement in an electric field shows that the particles must be charged electrically, a double layer probably being formed at their surfaces, in accordance with Quincke's theory of electric endosmose. The reversal of direction implies a reversal of sign in the charges on the particles, and therefore, by slowly adding acid or alkali to the liquid, it is possible to obtain an iso-electric point at which there is no potential difference between the liquid and the particles. Hardy finds that as this point is approached, the stability of the system diminishes, and at the iso-electric point it is probable that coagulation spontaneously occurs. The same observer has also discovered that, in the case of colloids travelling with the electric current, it is the anion which is active in causing coagulation, and not the metallic ion as in the experiments of

[1] *Jour. Physiol.* XXIV. 288 (1899); *Proc. R. S.* LXVI. 110 (1900).

Schulze, Prost, and Linder and Picton, who all used colloids which move against the current. Thus it is always the ion possessing a charge of opposite kind to that on the colloid particles that is effective in producing coagulation.

These observations suggest that the coagulative power of electrolytes may depend on a modification, under the electrostatic influence of the ionic charges, of the surface energy of the interface between the two phases of the colloidal system. As shown in the Chapter on contact electricity, the natural surface energy of such an interface is diminished by the presence of certain kinds of electric double layers. The tendency of the surface tension to condense many small particles into a few larger ones (p. 43) is thus reduced, and the system of small particles may become stable. Approach to the iso-electric point will, by decreasing the intensity of the double layer, increase the surface tension, and diminish the stability of the system, while the absorption of ions possessing charges of opposite sign to those on the particles will reduce the charges on the particles, and again act in a similar manner. The average size of the particles will be increased, and, if the influence at work is sufficient, the particles may be precipitated, or if enough colloid matter is present, the whole solution may coagulate into a more or less solid mass. As another mode of stating the explanation, we may say that a high potential difference implies a great mutual affinity between the two phases, tending to expand the interface. As the opposite charges of the electric double layer are annulled, the affinity diminishes; it vanishes at the iso-electric point, and the solution becomes unstable.

A different explanation of the coagulative properties of certain substances has been offered by Quincke[1], on the basis of changes of surface tension only. These changes are supposed to be produced by the spreading of the electrolytic solutions over the surfaces of the particles, forming a new interface with the surrounding liquid. This hypothesis makes no attempt to explain the relations of coagulative power with electrical conductivity and valency.

[1] *B. A. Report*, 1901, p. 60.

Nature of colloidal solutions.

Liquid solutions of colloids may be regarded either as ordinary solutions, of which the solutes possess enormously high molecular weights, or as systems of two phases, composed of suspensions of particles in the liquid, different from it and of greater than molecular dimensions. Much discussion has taken place on the relative merits of these two hypotheses. It is certain that some colloid solutions may be kept almost indefinitely without precipitation; but, if the foreign particles are small enough, the viscosity of the water is enough to make the settling process almost indefinitely slow. The properties of hydrosols differ considerably from those of true solutions; the rate of diffusion is very much less, the heat of solution is usually inappreciable or at all events very small, while no certain indications have been obtained of measurable osmotic pressures or depressions of the freezing point of the solvent.

In some colloid solutions, the presence of suspended particles can readily be detected. Picton and Linder[1], who have made extensive investigations on this subject, have observed a continuous gradation in size from particles large enough to be visible under a microscope. Such particles exist in solutions of mercuric sulphide and of arsenious sulphide prepared from the tartrate; under a magnification of 1000 diameters they appear as minute solid particles in rapid Brownian movement, crowded together so closely that very little free space is left. Other solutions of colloidal sulphides, together with those of ferric hydrate, chromic hydrate, aluminium hydrate, silicic acid, cellulose, starch, and acid and neutral Congo-red, while non-resolvable under the microscope, contain particles large enough to scatter and polarize a beam of lime-light. These optical methods fail to show the presence of particles in the colloidal solutions of molybdic acid, and of silicic acid in presence of hydrochloric acid. On the other hand, certain crystalloids possessing very complicated molecules, oxyhaemoglobin, carbonic oxide haemoglobin, and a compound of ferric hydrate with ferric chloride, which is said to crystallize as $9Fe_2O_3 . FeCl_3$, yield solutions which contain particles large enough to scatter

[1] *Jour. Chem. Soc. Trans.* LXI. 148 (1892).

and polarize light[1]. A colloidal solution of arsenic sulphide, prepared from the aqueous solution of pure arsenious acid, showed a diffusive power comparable with that of crystalloids, though the same solution polarized light. Picton and Linder conclude that there is no distinction in kind between colloid and crystalloid solution, but that a continuous gradation exists between solutions containing colloid particles visible under a microscope and electrolytic solutions of common crystalloid salts and acids. The absence of measurable osmotic-pressure properties appears to be merely an affair of arithmetic. Particles of a size to scatter light in accordance with the observations to which we have referred, must be comparable in size with the wave-length of light, about 5×10^{-5} centimetre. If the particles are close together we may conclude there are about 10^4 in a linear centimetre, or 10^{12} in a cubic centimetre. In a normal solution of a crystalloid which gives an osmotic pressure of about 22 atmospheres, the number of solute molecules is approximately 5×10^{20}. The osmotic pressure of the colloid solution in question will therefore be about 2×10^{-9} of that of a normal solution of a crystalloid, a value much too small to be measurable.

It is worthy of note that turbid suspensions of clay, kaoline, etc., in water are rapidly cleared by the addition of small quantities of metallic salts[2]. This action, which is almost certainly of the same nature as the coagulation studied above, probably helps in the formation of sand-banks at the mouths of rivers, the salts of the sea water clearing the suspensions of clay brought down by the fresh water; precipitation then occurs owing to the diminished velocity.

The conditions which determine the colloid or crystalloid nature of a substance are at present little understood. The persistence of the colloid properties when a substance passes from the dissolved to the non-dissolved state, shows that the

[1] Gamgee has shown in other ways that oxyhaemoglobin has a mixture of colloidal and crystalloidal properties. *Proc. R. S.* LXX. 79 (1902).

[2] Schulze, *Pogg. Ann.* CXXIX. 366 (1866); Schloesing, *Compt. Rend.* LXX. 1345 (1870); Bodlander, *Gött. Nachr.* 1893, p. 267; Spring, *Rec. Trav. Chim. Pays-Bas*, 1900, pp. 222, 294.

determining conditions must be of fundamental importance. The molecular forces seem to be much less active in colloids, but the freedom with which some of them disintegrate and dissolve in presence of water and other liquids indicates that some interaction between them and their solvent must occur. On these lines, making certain assumptions as to the nature of the forces at work and their variation with the distance, Donnan[1] has offered an investigation of the conditions which would secure the disintegration and solution of a colloid.

It seems likely that the forces and interactions which are involved in crystalloid solution are of the nature of those which are classed as chemical or molecular, while, when colloids dissolve, the actions between solvent and solute are conditioned also by the phenomena which are studied under the names of surface tension and capillarity. As the size of the dissolved aggregates or particles increases, the importance of the chemical forces diminishes and that of the capillary forces grows. In studying the properties of colloidal solutions by the light of the Phase Rule, we must remember that the surface of separation between the phases is enormously extended owing to the minute size of the particles, and the surface energy therefore becomes of great, perhaps of preponderating, importance. An investigation of the influence of capillarity on the theory of equilibrium will be found in Gibbs' work[2]; he shows that an interfacial transition layer provides in a sense a new phase coexistent with those on each side of it and having its own characteristic equation. Again, colloids may be regarded as undercooled liquids, and in a condition of unstable equilibrium. Their condition may therefore depend on the time, which introduces a new variable beyond those contemplated by the ordinary application of the Phase Rule[3].

In conclusion we may point out that, if colloid and crystalloid solution are but the extreme limits of a continuous series of phenomena, the study of dissolved colloids of varying degrees of aggregation promises to throw light on the general problem of the fundamental nature of solution.

[1] *Phil. Mag.* [6] I. 647 (1901). [2] *Trans. Connect. Acad.* III. 380 (1877).
[3] Bancroft, *The Phase Rule*, p. 234.

ADDITIONS.

Chapter III. p. 71. Solid solutions.

BRUNI and Padoa[1] have prepared solid solutions by the sublimation of a mixture of two crystalline substances, such as mercuric iodide and bromide. The mixture was placed at the bottom of a glass bulb, which was then partially exhausted and kept in a bath of alloy at a temperature a few degrees below the fusing point of the mixture. After a day or so, homogeneous crystals of a solid solution were found in the upper part of the bulb.

Chapter III. p. 75. Distillation of mixtures.

Lord Rayleigh[2] has measured the compositions of liquid and vapour in the distillation of mixtures, drawing curves with the two compositions as axes. With 96 per cent. alcohol the compositions were identical, in agreement with the minimum boiling point found by Noyes and Warfel[3]. By proper arrangements, separation of the mixture can be effected by a single continuous operation.

Chapter IV. p. 93. Solubility of mixtures.

Since the year 1897 a series of researches has been carried out by Van 't Hoff and his pupils on the solubility of simple salts, double salts, and mixtures, with the immediate object of elucidating the geological process involved in the formation of oceanic salt deposits, such as those of Stassfurt[4].

[1] *Atti Accad. dei Lincei, Roma*, XI. 565 (1902).

[2] *Phil. Mag.* [6] IV. 521 (Nov. 1902).

[3] *Amer. Chem. Soc. Jour.* XXIII. 463 (1901).

[4] A report on the work was communicated by E. F. Armstrong to the British Association (1901, p. 262); the original papers will be found in the *Abhand. Kön. Akad. Wissensch.*, Berlin, 1897—1902.

When several salts are simultaneously present, the possible number of solids in equilibrium with the solution may be predicted by the Phase Rule, but the nature of any double salts, the possibility of their co-existence, and the order in which the various solids appear, must be determined by experiment.

As an example we may take a solution containing potassium chloride KCl and magnesium chloride $MgCl_2 . 6H_2O$, substances which form a double salt of composition $KCl . MgCl_2 . 6H_2O$ called Carnallite. Here we have three components, namely, water and the two simple salts; the double salt, not being an independent variable, is merely a possible solid phase. To obtain a monovariant system, which is in equilibrium at one given temperature when the pressure is fixed, we must assemble four phases, two being solids. Working at the constant pressure of the atmosphere, and at a constant temperature of 25°, the conditions of such a system are completely determined, and the liquid phase can have only one composition. When, at the beginning of the deposition, the only solid phase is composed of the crystals of the less soluble salt, the system is not determined, and the composition of the liquid will vary as evaporation proceeds till a new solid phase appears. The composition of the liquid phase then remains constant as long as both solids are deposited. The phenomena may be repre-

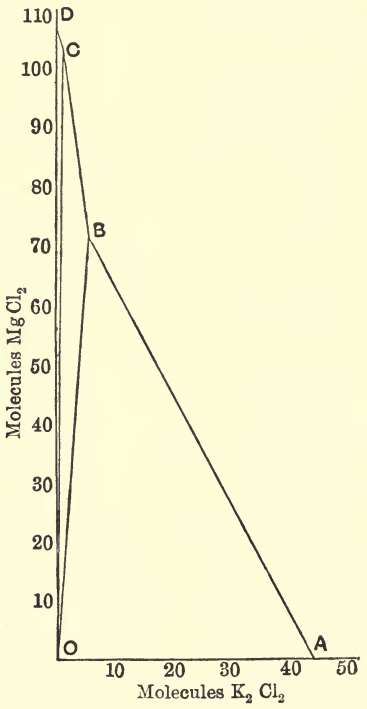


Fig. 66.

sented on a diagram (Fig. 66), for which the necessary data are given in the following table, the amount of potassium chloride being reckoned in double molecules as K_2Cl_2, for the sake of comparison with $MgCl_2$.

Substances saturating the solution	Points on the diagram	Number of molecules per thousand molecules of water	
		K_2Cl_2	$MgCl_2$
KCl	A	44	0
KCl and Carnallite	B	5·5	72·5
Carnallite and $MgCl_2.6H_2O$	C	1	105
$MgCl_2.6H_2O$	D	0	108

Points lying inside the lines *ABCD* represent the composition of unsaturated solutions; points on the line *AB* indicate the number of double molecules of potassium chloride which saturate the liquid as the amount of magnesium chloride is increased; similarly the lines *BC* and *CD* represent the conditions of saturation with Carnallite and magnesium chloride respectively. The points *B* and *C*, representing the composition of solutions simultaneously saturated with two solid phases, are determined by the experimental results given in the table.

In more complicated systems the number of variables can often be reduced by remembering that in what are known as reciprocal salt pairs, for example,

$$MgCl_2 + K_2SO_4 = K_2Cl_2 + MgSO_4,$$

the amount of the second pair can be expressed in terms of the amount of the first. This consideration makes it often possible to represent on a solid model the phenomena observed when several salts are present.

By studying the evaporation of sea water on these lines, it has been found that the order in which salts should be deposited is probably as follows. (1) Sodium Chloride; (2) Sodium Chloride and Magnesium Sulphate; (3) Sodium Chloride and Leonite; (4) Sodium Chloride, Leonite, and Potassium Chloride, or Sodium Chloride and Kainite; (5) Sodium Chloride, Kieserite and Carnallite; (6) Sodium Chloride, Kieserite, Carnallite,

and Magnesium Chloride, the solution then drying up without further change of composition.

This succession agrees with that found on actually evaporating sea water at 25°, and approximately conforms to that observed in the geological deposits at Stassfurt.

Chapter V. p. 96. Semi-permeable membranes.

Morse and Horn[1] precipitated a membrane of copper ferrocyanide in the walls of a porous cell by placing solutions of copper sulphate and potassium ferrocyanide on each side of the wall, and passing an electric current till the resistance became 1500 to 3000 ohms. Membranes thus obtained easily withstood pressures of four or five atmospheres.

Chapter IX. p. 224. Ionic Viscosity.

It has been shown by Lyle and Hosking[2] that, when plotted with the temperature, the equivalent conductivity and the fluidity of solutions of sodium chloride give similar but not identical curves, which indicate that both conductivity and fluidity would vanish at a temperature of $-35°{\cdot}5$ Centigrade.

Chapter XII. pp. 332 and 363. Effect on conductivity of the nature of the solvent.

The conductivity of solutions of salts etc. dissolved in liquid hydrocyanic acid has been investigated by Kahlenberg and Schlundt[3]. The potassium salts have conductivities about three times those of the corresponding aqueous solutions. These aqueous solutions are themselves highly ionized, so that the increased conductivity in hydrocyanic acid must be due to the smaller ionic viscosity of that solvent. In light of the high dielectric constant (about 95) of the liquid, it is interesting to observe that some other salts showed less conductivity than in water, and that both water and alcohol were found to dissolve to form non-conducting solutions. (See p. 362.)

[1] *Amer. Chem. Jour.* XXVI. 80 (1901).
[2] *Phil. Mag.* [6] III. 487 (1902).
[3] *Jour. Phys. Chem.* VI. 447 (1902).

TABLE OF ELECTRO-CHEMICAL PROPERTIES OF AQUEOUS SOLUTIONS,

COMPILED BY THE

REV. T. C. FITZPATRICK, M.A.,

FELLOW OF CHRIST'S COLLEGE, CAMBRIDGE,

and Reprinted, by permission, from the Report of the British Association for the Advancement of Science, 1893.

THE comparison of the numerical results of electrolytic observations is rendered difficult by the fact that the data are scattered in various periodicals and expressed by different observers in units that are not comparable without considerable labour. The following table has been compiled with the object of facilitating the comparison.

In the table are included all observations known to the compiler, with the exception that a selection only is made in the case of organic bodies. Observations for a number of additional substances will be found in Ostwald's papers in the *Journal für Chemie*, vols. xxxi., xxxii., and xxxiii., and in the *Zeitschrift für physikalische Chemie*, vol. i. With this restriction it is hoped that no important observations published before the year 1893 have been omitted, and that, in the reduction of results, expressed in such varied units, the table is sufficiently free from mistakes for it to be of service. The data included refer to the strength and specific gravity of solutions, with the corresponding conductivities, migration constants, and fluidities. The several columns are as follows:—

I. Percentage composition, *i.e.* the number of parts by weight of the salt (as represented by the chemical formula) in 100 parts of the solution.

II. The number of gramme equivalents per litre, *i.e.* the number of grammes of the salt per litre divided by the chemical equivalent in grammes, as given for each salt.

III. The specific gravities of the solutions: in most cases the specific gravities of the solutions are not given by the observers, and the numbers given have been deduced from Gerlach's tables in the *Zeitschrift für analytische Chemie*, vol. viii. p. 243, &c.

IV. The temperatures at which the solutions have the specific gravities given in the previous column for the given strength of solution.

V. The conductivity, as expressed by the observer. In the cases in which the observer has expressed his results for specific equivalent conductivity no numbers are given in this column.

VI. The temperature at which the conductivities of the solutions have been determined.

VII. The temperature coefficient referred to the conductivity at 18°, *i.e.* $\frac{1}{k_{18}}\left(\frac{\delta k_{18}}{\delta t}\right)$.

VIII. The specific equivalent conductivity of the solutions at 18° in terms of the conductivity of mercury at 0°; the specific equivalent conductivity is the conductivity of a column of the liquid 1 centimetre long and 1 square centimetre in section, divided by the number of gramme equivalents per litre.

In some few cases, in which no temperature coefficients have been determined, the results have been given for the temperature at which the observations were made.

The numbers given in the column are the values for the specific equivalent conductivity $\times 10^9$.

IX. This column contains the values for specific equivalent conductivity at 18° in C.G.S. units: they are obtained from those in the previous column by being multiplied by the value of the conductivity of mercury at 0° in C.G.S. units. The factor is $1{\cdot}063 \times 10^{-5}$. The values in Kohlrausch's units, reciprocal ohms $\times$ centimetre cube per gram equivalent of salt per cubic centimetre, can be obtained by dividing by 10 the numbers actually given in the column (*i.e.* 1293 becomes 129·3 for the first solution of potassium chloride, &c.). The results may in some cases differ by a few parts in a thousand from Kohlrausch's latest values given in his book *das Leitvermögen der Elektrolyte* (Leipzig, 1898).

UNIVERSITY OF CALIFORNIA

X. The migration constant for the anion; for instance, in the case of copper sulphate ($CuSO_4$), for (SO_4). Some more recent results are given on p. 212.

XI. The temperatures at which the migration constants have been determined.

XII. The number of gramme equivalents per litre, as defined for column II., for which the fluidity data are given in the following columns.

XIII. The fluidity of the solutions of the strength given in the previous column.

Most of the results given for the fluidity of solutions are expressed in terms of the fluidity of water at the same temperature; to obtain the absolute values for the solutions they have been multiplied by the value for the fluidity of water at the given temperature. The values used for this purpose have been taken from Sprung's observations for the viscosity of water given in *Poggendorff's Annalen*, vol. clix. p. 1.

To obtain the values for fluidity in c.g.s. units, the numbers in this column must be multiplied by the factor ·1019.

XIV. The temperature at which the solutions have the fluidity given in the previous column.

XV. The temperature coefficient of fluidity at 18°, that is $\frac{1}{f_{18}}\left(\frac{\delta f_{18}}{\delta t}\right)$.

XVI. In the last column are given the references to the various papers from which the data are taken: against each reference will be found a number, which appears also against the first of the data which have been taken from the paper in question.

Hydrochloric Acid.

Equivalent Gramme Molecule, HCl, 36·46.

Composition				Conductivity Data					Migration Data		Fluidity Data				Notes
Percentage Composition	Equivalent Gramme Molecules per Litre	Specific Gravity	Temperature	Conductivity in Observer's Units	Temperature	Temperature Coefficient	Specific Equivalent Conductivity at 18° in terms of Mercury $\times 10^8$	Specific Equivalent Conductivity at 18° in C.G.S. Units $\times 10^{13}$	n	Temperature	Equivalent Gramme Molecules per Litre	Fluidity $\times 10^2$	Temperature	Temperature Coefficient	
			°		°					°			°		
·0000364	·00001	—	—	—	18	—	1254[1]	1333	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000073	·00002	—	—	—	18	—	2057	2186	—	—	—	—	—	—	
·000219	·00006	—	—	—	18	—	2968	3155	—	—	—	—	—	—	
·000364	·0001	—	—	—	18	—	3171	3371	—	—	—	—	—	—	
·00073	·0002	—	—	—	18	—	3340	3550	—	—	—	—	—	—	[2] Ostwald, *Journal für Chemie*, vol. xxxi. p. 437.
·00219	·0006	—	—	—	18	—	3440	3656	—	—	—	—	—	—	
·00364	·001	—	—	—	18	—	3455	3672	—	—	—	—	—	—	
·0073	·002	—	—	—	18	—	3455	3672	—	—	—	—	—	—	
·0219	·006	—	—	—	18	—	3438	3654	—	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 395.
·0364	·01	—	—	—	18	·0159	3416	3631	—	—	—	—	—	—	
·047	·0128	1·0002	5·5	—	—	—	—	—	·210[3]	—	—	—	—	—	
·109	·03	—	—	—	18	—	3369	3581	—	—	1·54	929[4]	20	·0239	
·182	·05	—	—	—	18	—	3330	3540	—	—	2·87	850	20	·0214	[4] Grotian, *Pogg. Annal.* vol. clx. p. 262.
·31	·085	1·0016	7·8	—	—	—	—	—	·216	—	6·03	736	20	·0190	
·364	·1	1·0012	15·5	—	18	—	3244	3448	—	—	9·47	570	20	·0185	
·704	—	—	—	—	—	—	—	—	·171	—	—	—	—	—	
1·2	·33	1·0062	7·6	—	—	—	—	—	·161	—	—	—	—	—	
1·807	·5	1·0086	15·5	—	18	—	3017	3207	—	—	—	—	—	—	
2·68	·744	1·0139	7·6	—	—	—	—	—	·168	—	—	—	—	—	
3·58	1·0	1·0179	15·5	—	18	—	2780	2955	—	—	—	—	—	—	
9·20	2·64	1·0472	7·4	—	—	—	—	—	·193	—	—	—	—	—	
10·41	3·0	1·0501	15·5	—	18	—	2010	2136	—	—	—	—	—	—	
16·8	5·0	1·0832	15·5	—	18	—	1420	1509	—	—	—	—	—	—	
25·59	—	—	—	—	—	—	—	—	·319	—	—	—	—	—	
31·5	10·0	1·1552	15·5	—	18	—	600	638	—	—	—	—	—	—	
·000225	·000061	—	—	83·22[2]	25	—	—	3381	—	—	—	—	—	—	
·00045	·000122	—	—	86·6	25	—	—	3519	—	—	—	—	—	—	
·00089	·000244	—	—	88·6	25	—	—	3601	—	—	—	—	—	—	
·00178	·000488	—	—	89·5	25	—	—	3637	—	—	—	—	—	—	
·00355	·000975	—	—	89·5	25	—	—	3637	—	—	—	—	—	—	
·0071	·00195	—	—	89·6	25	—	—	3641	—	—	—	—	—	—	
·0142	·0039	—	—	89·2	25	—	—	3625	—	—	—	—	—	—	
·0285	·0078	—	—	88·7	25	—	—	3605	—	—	—	—	—	—	
·057	·0156	—	—	88·1	25	—	—	3580	—	—	—	—	—	—	
·114	·0312	—	—	87·0	25	—	—	3535	—	—	—	—	—	—	
·228	·0625	—	—	85·4	25	—	—	3470	—	—	—	—	—	—	
·456	·125	—	—	83·6	25	—	—	3397	—	—	—	—	—	—	

·907	·25	1·0045	15·5	80·9	25	—	—	3268	—	—	—	—	—	—	[5] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
1·807	·5	1·0086	15·5	77·9	25	—	—	3166	—	—	—	—	—	—	
·0286	·00784	—	—	2·66[5]	18	—	3395	3609	—	—	—	—	—	—	
·057	·0157	—	—	5·28	18	—	3369	3581	—	—	—	—	—	—	
·114	·0314	—	—	10·4	18	—	3323	3532	—	—	—	—	—	—	
·228	·0627	—	—	20·6	18	—	3289	3496	—	—	—	—	—	—	
·456	·1255	1·0018	15·5	40·5	18	—	3234	3438	—	—	—	—	—	—	
·910	·251	1·0046	15·5	78·7	18	—	3138	3336	—	—	—	—	—	—	
1·813	·502	1·0090	15·5	151·3	18	—	3014	3204	—	—	—	—	—	—	

Potassium Chloride.

Equivalent Gramme Molecule, KCl, 74·59.

·0000746	·00001	—	—	—	18	—	1216[1]	1293	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000149	·00002	—	—	—	18	—	1217	1294	—	—	—	—	—	—	
·000448	·00006	—	—	—	18	—	1212	1288	—	—	—	—	—	—	
·000746	·0001	—	—	—	18	—	1209	1285	—	—	—	—	—	—	
·00149	·0002	—	—	—	18	—	1209	1285	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. xcviii. p. 27.
·00448	·0006	—	—	—	18	—	1199	1275	—	—	—	—	—	—	
·00746	·001	—	—	—	18	—	1193	1268	—	—	—	—	—	—	
·0149	·002	—	—	—	18	—	1185	1260	—	—	·125	992[3]	20	—	
·0448	·006	—	—	—	18	—	1162	1235	—	—	·25	995	20	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
·0746	·01	—	—	—	18	·0221	1147	1219	—	—	·5	997	20	—	
·224	·03	—	—	—	18	—	1107	1178	·503[2]	—	1·0	997	20	—	
·372	·05	1·0019	15	—	18	—	1083	1151	—	—	1·466	987[4]	20	·0219	
·743	·1	1·0046	15	—	18	—	1047	1113	—	—	3·432	956	20	·0191	[4] Sprung, *Pogg. Annal.* vol. clix. p. 1.
3·64	·5	1·0228	15	—	18	·0206	958	1018	—	—	—	—	—	—	
5·15	·714	1·0342	7·2	—	—	—	—	—	·515	—	·0625	986[5]	20	—	
7·13	1·0	1·0457	18	—	18	·0199	919	977	—	—	·125	986	20	—	[5] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
13·1	1·94	1·1034	4·5	—	—	—	—	—	·516	—	·25	987	20	—	
17·1	2·55	1·1155	12·4	—	—	—	—	—	·516	—	·5	988	20	—	
19·7	3·0	1·1359	15	—	18	·0170	827	879	—	—	1·0	990	20	—	[6] Bouty, *Journal de Physique*, vol. vi. p. 10.
·00746	·001	—	—	1·29[6]	18	—	—	1250	—	—	1·0	997[7]	20	—	
·0746	·01	—	—	12·1	18	—	—	1206	—	—	—	—	—	—	
·743	·1	1·0046	15	113·0	18	—	—	1130	—	—	—	—	—	—	[7] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
1·48	·2	1·0096	15	220·0	18	—	—	1100	—	—	—	—	—	—	
3·74	·5	1·0228	15	508·0	18	—	—	1016	—	—	—	—	—	—	
7·13	1·0	1·0457	15	991·0	18	—	—	991	—	—	—	—	—	—	
13·7	2·0	1·0912	15	1888·0	18	—	—	944	—	—	—	—	—	—	
9·7	3·0	1·1359	15	2742·0	18	—	—	914	—	—	—	—	—	—	

Potassium Chloride—*continued.*

Equivalent Gramme Molecule, KCl, 74·59.

			°		°					°				°		
·00725	·000976	—	—	142·3[8]	25	·0221	—	1310	—	—	—	—	—	—	—	[8] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·0145	·00195	—	—	138·6	25	—	—	1276	—	—	—	—	—	—	—	
·029	·0039	—	—	134·8	25	—	—	1241	—	—	—	—	—	—	—	
·058	·0078	—	—	131·1	25	—	—	1207	—	—	—	—	—	—	—	[9] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·116	·0156	—	—	127·6	25	—	—	1174	—	—	—	—	—	—	—	
·232	·0312	1·0008	15	124·2	25	—	—	1143	—	—	—	—	—	—	—	
·0072	·00097	—	—	—	18	·0236	1180[9]	1254	—	—	—	—	—	—	—	
·0142	·0019	—	—	—	18	·0231	1140	1211	—	—	—	—	—	—	—	
·0283	·0038	—	—	—	18	·0222	1110	1180	—	—	—	—	—	—	—	
·0746	·0100	—	—	—	18	·0220	1080	1148	—	—	—	—	—	—	—	
·137	·0184	—	—	—	18	·0218	1060	1127	—	—	—	—	—	—	—	

Ammonium Chloride.

Equivalent Gramme Molecule, NH_4Cl, 53·5.

·0000535	·00001	—	—	—	18	—	1205[1]	1281	—	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000107	·00002	—	—	—	18	—	1209	1285	—	—	—	—	—	—	—	
·000321	·00006	—	—	—	18	—	1215	1292	—	—	—	—	—	—	—	
·000535	·0001	—	—	—	18	—	1209	1285	—	—	—	—	—	—	—	
·00107	·0002	—	—	—	18	—	1204	1280	—	—	—	—	—	—	—	[2] Sprung, *Pogg. Annal.* vol. clix. p. 1.
·00321	·0006	—	—	—	18	—	1197	1273	—	—	—	—	—	—	—	
·00535	·001	—	—	—	18	—	1190	1265	—	—	·693	989[2]	20	—	—	
·0107	·002	—	—	—	18	—	1180	1255	—	—	1·625	1009	20	—	—	[3] Grotian, *Pogg. Annal.* vol. clx. p. 262.
·0321	·006	—	—	—	18	—	1157	1230	—	—	3·069	1005	20	—	—	
·0535	·01	—	—	—	18	·0226	1142	1214	—	—	4·666	980	20	—	—	
·1605	·03	—	—	—	18	—	1101	1171	—	—	—	—	—	—	—	[4] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·267	·05	1·0002	15·0	—	18	—	1078	1146	—	—	·95	996[3]	20	·0229	—	
·534	·1	1·0013	15·0	—	18	—	1035	1100	—	—	1·925	985	20	·0212	—	
·57	·107	1·0019	7·0	—	—	—	—	—	·508[5]	—	2·93	1011	20	·0198	—	
2·65	·5	1·0084	15·0	—	18	·0204	948	1007	—	—	3·956	987	20	·019	—	
3·44	·65	1·0113	9·8	—	—	—	—	—	·514	—	—	—	—	—	—	[5] Hittorf, *Pogg. Annal.* vol. xcviii. p. 33.
5·263	1·0	1·0165	15·0	—	18	·0198	907	964	—	—	1·0	998[4]	20	—	—	
7·59	1·45	1·0241	9·8	—	—	—	—	—	·514	—	—	—	—	—	—	
—	3·0	1·0461	15·0	—	18	·0172	825	877	—	—	—	—	—	—	—	
15·92	3·12	1·0483	11·8	—	—	—	—	—	·517	—	—	—	—	—	—	
—	5·0	1·0730	15·0	—	18	·0155	752	799	—	—	—	—	—	—	—	

·334	·0625	1·0005	15·0	65·9[6]	18	—	1054	1120	—	—	—	—	—	—	[6] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi. No. 3.
·667	·125	1·0018	15·0	127·5	18	—	1020	1084	—	—	—	—	—	—	
1·331	·25	1·0042	15·0	244·0	18	—	976	1037	—	—	—	—	—	—	
2·65	·5	1·0084	15·0	466·0	18	—	932	991	—	—	—	—	—	—	
·0081	·00152	—	—	—	18	·0233	1200[7]	1276	—	—	—	—	—	—	[7] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0151	·00282	—	—	—	18	·0226	1150	1222	—	—	—	—	—	—	
·0309	·00578	—	—	—	18	·0224	1120	1190	—	—	—	—	—	—	
·053	·0099	—	—	—	18	·0224	1090	1159	—	—	—	—	—	—	
·0942	·0176	—	—	—	18	·0221	1060	1127	—	—	—	—	—	—	
·183	·0342	—	—	—	18	·0221	1030	1095	—	—	—	—	—	—	

Sodium Chloride.

Equivalent Gramme Molecule, NaCl, 58·5.

·000058	·00001	—	—	—	18	—	1024[1]	1088	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000117	·00002	—	—	—	18	—	1028	1093	—	—	—	—	—	—	
·000351	·00006	—	—	—	18	—	1027	1092	—	—	—	—	—	—	
·000585	·0001	—	—	—	18	—	1029	1094	—	—	—	—	—	—	
·00117	·0002	—	—	—	18	—	1018	1082	—	—	1·437	854[2]	20	·0245	[2] Sprung, *Pogg. Annal.* vol. clix. p. 13.
·00351	·0006	—	—	—	18	—	1014	1077	—	—	2·704	740	20	·0243	
·00585	·001	—	—	—	18	—	1008	1071	—	—	5·013	558	20	·0252	
·0117	·002	—	—	—	18	—	998	1061	—	—	—	—	—	—	[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·0351	·006	—	—	—	18	—	976	1037	—	—	—	—	—	—	
·0585	·01	—	—	—	18	·0238	962	1023	—	—	1·0	896[3]	20	—	
·1755	·03	1·0006	15·0	—	18	—	920	978	—	—	—	—	—	—	
·292	·05	1·0015	15·0	—	18	—	897	953	—	—	—	—	—	—	
·31	·055	1·0023	5·6	—	—	—	—	—	·622[5]	—	·0625	980[4]	20	—	[4] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
·583	·1	1·0038	15·0	—	18	—	865	919	—	—	·125	975	20	—	
·945	·162	1·0068	17·4	—	—	—	—	—	·628	—	·25	963	20	—	
2·865	·5	1·0207	15·0	—	18	·0220	757	804	—	—	·5	942	20	—	[5] Hittorf, *Pogg. Annal.* vol. cvi. p. 374.
4·61	·814	1·0334	16·2	—	—	—	—	—	·634	—	1·0	890	20	—	
5·62	1·0	1·0406	15·0	—	18	·0218	695	739	—	—	—	—	—	—	[6] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
15·03	2·867	1·1159	8·6	—	—	—	—	—	·647	—	—	—	—	—	
15·71	3·0	1·1171	15·0	—	18	·0213	528	561	—	—	—	—	—	—	
22·34	4·477	1·1716	13·0	—	—	—	—	—	·648	—	—	—	—	—	
24·6	5·0	1·1890	15·0	—	18	·0227	398	423	—	—	—	—	—	—	
·365	·0625	1·0021	15·0	54·2[6]	18	—	867	921	—	—	—	—	—	—	
·728	·125	1·0050	15·0	104·2	18	—	834	886	—	—	—	—	—	—	

Sodium Chloride—*continued.*

Equivalent Gramme Molecule, NaCl, 58·5.

			°		°					°			°		
1·44	·25	1·0105	15·0	197·6	18	—	790	840	—	—	—	—	—	—	[7] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 80.
2·86	·5	1·0207	15·0	369·0	18	—	738	784	—	—	—	—	—	—	
·0058	·000976	—	—	119·5[7]	25	—	—	1089	—	—	—	—	—	—	
·0115	·00195	—	—	116·3	25	—	—	1060	—	—	—	—	—	—	[8] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·023	·0039	—	—	112·1	25	—	—	1021	—	—	—	—	—	—	
·046	·0078	—	—	110·1	25	—	—	1003	—	—	—	—	—	—	
·092	·0156	—	—	107·0	25	—	—	975	—	—	—	—	—	—	
·183	·0312	1·0006	15·0	104·0	25	—	—	948	—	—	—	—	—	—	
·00643	·0011	—	—	—	18	·0236	970[8]	1031	—	—	—	—	—	—	
·00936	·0016	—	—	—	18	·0232	950	1010	—	—	—	—	—	—	
·0287	·0049	—	—	—	18	·0232	920	978	—	—	—	—	—	—	

Lithium Chloride.

Equivalent Gramme Molecule, LiCl, 42·5.

·0000425	·00001	—	—	—	18	—	965[1]	1026	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000085	·00002	—	—	—	18	—	955	1015	—	—	—	—	—	—	
·000255	·00006	—	—	—	18	—	945	1004	—	—	—	—	—	—	
·000425	·0001	—	—	—	18	—	943	1002	—	—	—	—	—	—	
·00085	·0002	—	—	—	18	—	938	997	—	—	—	—	—	—	[2] Sprung, *Pogg. Annal.* vol. clix. p. 17.
·00255	·0006	—	—	—	18	—	926	984	—	—	1·908	741[2]	20	·0252	
·00425	·001	—	—	—	18	—	921	979	—	—	3·54	584	20	·0248	
·0085	·002	—	—	—	18	—	911	968	—	—	7·365	313	20	·0247	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 38.
·0255	·006	—	—	—	18	—	889	945	—	—	—	—	—	—	
·0425	·01	—	—	—	18	·0232	875	930	—	—	—	—	—	—	
·1275	·03	—	—	—	18	—	834	887	—	—	·125	957[3]	20	—	
—	·042	—	—	—	—	—	—	—	·674[5]	—	·25	937	20	—	[4] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·212	·05	1·0006	15	—	18	—	811	862	—	—	·5	907	20	—	
·424	·1	1·0021	15	—	18	—	775	824	—	—	1·0	863	20	—	
—	·11	—	—	—	—	—	—	—	·699	—	—	—	—	—	
—	·235	—	—	—	—	—	—	—	·718	—	—	—	—	—	
2·985	·5	1·0126	15	—	18	·0229	661	703	—	—	1·0	857[4]	20	—	[5] Kuschel, *Wied. Annal*, vol. xiii. p. 295.
—	·809	—	—	—	—	—	—	—	·739	—	—	—	—	—	
4·146	1·0	1·0249	15	—	18	·0225	591	628	—	—	—	—	—	—	
7·757	1·784	—	—	—	—	—	—	—	·738	—	—	—	—	—	

12·0	3·0	1·0700	15	—	18	·0218	421	447	—	—	—	—	—	—	[6] Fitzpatrick, *Phil. Mag.* (5th series), vol. xxiv. p. 377.
13·91	3·213	—	—	—	—	—	—	—	·753	—	—	—	—	—	
19·12	5·0	1·1110	15	—	18	·0220	303	322	—	—	—	—	—	—	
26·93	6·895	—	—	—	—	—	—	—	·773	—	—	—	—	—	
34·91	10·0	1·2173	15	—	18	·0251	106	113	—	—	—	—	—	—	
·0083	·00195	—	—	—	18	—	897[6]	954	—	—	—	—	—	—	
·0165	·0039	—	—	—	18	·0234	882	938	—	—	—	—	—	—	
·0331	·0078	—	—	—	18	—	874	929	—	—	—	—	—	—	
·0662	·0156	—	—	—	18	—	849	902	—	—	—	—	—	—	
·1325	·0312	—	—	—	18	—	820	871	—	—	—	—	—	—	
·265	·0625	—	—	—	18	—	784	833	—	—	—	—	—	—	
·53	·125	1·0028	15	—	18	—	745	792	—	—	—	—	—	—	
1·056	·25	1·0063	15	—	18	—	694	738	—	—	—	—	—	—	

Strontium Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}SrCl_2$, 79·02.

·00506	·00064	—	—	—	18	·0244	1070[1]	1137	—	—	·969	867[2]	20	·0244	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0069	·00087	—	—	—	18	—	1040	1105	—	—	1·41	772	20	·0235	
·0111	·0014	—	—	—	18	·0240	1000	1063	—	—	3·31	611	20	—	
·0229	·0029	—	—	—	18	·0237	880	935	—	—	5·508	400	20	—	[2] Sprung, *Pogg. Annal.* vol. clix. p. 18.
—	·5	—	—	353[5]	18	·0217	706	—	—	—	·125	954[3]	20	—	[3] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
—	1·0	—	—	640	18	·0212	640	—	—	—	·25	923	20	—	
—	1·5	—	—	882	18	·0208	588	—	—	—	·5	860	20	—	
—	2·0	—	—	1082	18	·0204	541	—	—	—	1·0	752	20	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.
—	2·5	—	—	1250	18	—	500	—	—	—	—	—	—	—	
—	3·0	—	—	1387	18	—	462	—	—	—	·125	960[4]	20	—	[5] Kohlrausch, *Wied. Annal.* vol. vi. p. 148.
—	3·5	—	—	1499	18	—	426	—	—	—	·25	941	20	—	
—	—	—	—	—	—	—	—	—	—	—	·5	911	20	—	
—	—	—	—	—	—	—	—	—	—	—	1·0	853	20	—	

Barium Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}BaCl_2$, 104.

·000104	·00001	—	—	—	18	—	1142[1]	1214	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000208	·00002	—	—	—	18	—	1144	1216	—	—	·783	898[2]	20	·0240	
·000624	·00006	—	—	—	18	—	1133	1204	—	—	1·715	807	20	·0226	
·00104	·0001	—	—	—	18	—	1126	1197	—	—	2·955	683	20	·0222	[2] Sprung, *Pogg. Annal.* vol. clix. p. 18.
·00208	·0002	—	—	—	18	—	1118	1189	—	—	—	—	—	—	

Barium Chloride—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}BaCl_2$, 104.

			°		°				°			°		
·00624	·0006	—	—	—	18	—	1102	1172	—	—	1·0	883[3]	20	—
·0104	·001	—	—	—	18	—	1092	1161	—	—	—	—	—	—
·0208	·002	—	—	—	18	—	1074	1142	—	—	·125	963[4]	20	—
·0624	·006	—	—	—	18	—	1031	1096	—	—	·25	951	20	—
·104	·01	1·0001	15·0	—	18	·0234	1006	1069	—	—	·5	923	20	—
·311	·03	1·0022	15·0	—	18	—	939	998	—	—	1·0	868	20	—
·518	·05	1·0044	15·0	—	18	—	904	961	—	—	—	—	—	—
·784	·076	1·0070	9·6	—	—	—	—	—	·61[6]	—	·0625	970[5]	20	—
1·03	·1	1·0094	15·0	—	18	—	861	915	—	—	·125	955	20	—
1·24	·12	1·0112	19·7	—	—	—	—	—	·616	—	·25	926	20	—
4·97	·5	1·0457	15·0	—	18	·0214	725	771	—	—	·5	867	20	—
9·54	1·0	1·0905	15·0	—	18	·0207	658	699	—	—	1·0	760	20	—
10·65	1·13	1·1028	19·0	—	—	—	—	—	·642	—	—	—	—	—
21·6	2·55	1·2277	14·4	—	—	—	—	—	·663	—	—	—	—	—
23·5	2·88	1·2546	7·3	—	—	—	—	—	·664	—	—	—	—	—
—	3·0	1·2655	15·0	—	18	·0193	487	518	—	—	—	—	—	—

[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.

[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 35.

[5] Mutzel, *Wied. Annal.* vol. xliii. p. 25.

[6] Hittorf, *Pogg. Annal.* vol. cvi. p. 379.

Calcium Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}CaCl_2$, 55·46.

·434	·078	1·0036	20·0	—	—	—	—	—	·683[2]	—	—	—	—	—
·718	·13	1·0062	9·0	—	—	—	—	—	·673	—	—	—	—	—
2·71	·5	1·0231	15·0	348·0	18	·0218	696[1]	740	—	—	—	—	—	—
4·56	·853	1·0382	20·0	—	—	—	—	—	·683	—	3·098	630[3]	20	·0232
5·307	1·0	1·0451	15·0	633·0	18	·0213	633	673	—	—	7·437	251	20	·0235
10·19	2·0	1·0887	15·0	1083·0	18	·0207	542	576	—	—	9·984	111·4	20	·0309
14·71	3·0	1·1309	15·0	1389·0	18	·0203	463	492	—	—	—	—	—	—
18·93	4·0	1·1718	15·0	1583·0	18	·0201	398	423	—	—	·125	959[4]	20	—
20·2	4·3	1·1819	20·8	—	—	—	—	—	·727	—	·25	942	20	—
22·88	5·0	1·2119	15·0	1666·0	18	·0202	333	354	—	—	·5	906	20	—
26·6	6·0	1·2510	15·0	1644·0	18	·0206	274	291	—	—	1·0	844	20	—
26·73	6·04	1·2529	9·7	—	—	—	—	—	·749	—	—	—	—	—
29·75	6·91	1·2884	2·8	—	—	—	—	—	·765	—	·125	952[5]	20	—
30·11	7·0	1·2892	15·0	1541·0	18	·0216	220	234	—	—	·25	922	20	—
32·6	7·73	1·3160	12·4	—	—	—	—	—	·771	—	·5	858	20	—
33·37	8·0	1·3267	15·0	1370·0	18	·0231	171	182	—	—	1·0	751	20	—
36·6	9·0	1·3633	15·0	1177·0	18	·0244	130	138	—	—	—	—	—	—
37·08	9·14	1·3637	20·0	—	—	—	—	—	·78	—	—	—	—	—

[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 148.

[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 381.

[3] Sprung, *Pogg. Annal.* vol. clix. p. 19.

[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.

[5] Mutzel, *Wied. Annal.* vol. xliii. p. 25.

·00549	·00099	—	—	—	18	—	990[6]	1052	—	—	—	—	—	—	[6] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0089	·0016	—	—	—	18	—	970	1031	—	—	—	—	—	—	
·015	·0027	—	—	—	18	—	930	989	—	—	—	—	—	—	
·017	·00312	—	—	32·67	18	—	1043	1109	—	—	—	—	—	—	[7] Fitzpatrick, *Phil. Mag.* (5th series), vol. xxvi. p. 377.
·034	·00625	—	—	63·0	18	—	1008	1071	—	—	—	—	—	—	
·069	·0125	—	—	120·2	18	—	972	1033	—	—	—	—	—	—	
·138	·025	—	—	228·0	18	—	912	969	—	—	—	—	—	—	
·277	·05	1·0017	15·0	430·5	18	—	861	915	—	—	—	—	—	—	
·552	·1	1·0043	15·0	809·0	18	—	809	860	—	—	—	—	—	—	
1·1	·2	1·0093	15·0	1442·0	18	—	721	766	—	—	—	—	—	—	

MAGNESIUM CHLORIDE.

Equivalent Gramme Molecule, $\frac{1}{2}MgCl_2$, 47·46.

·0046	·000975	—	—	119·9[1]	25	—	—	1070	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 109.
·0092	·00195	—	—	115·8	25	—	—	1043	—	—	—	—	—	—	
·0185	·0039	—	—	111·6	25	—	—	1010	—	—	·125	1071[5]	25	—	
·037	·00781	—	—	107·2	25	—	—	972	—	—	·25	1046	25	—	[2] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 194.
·074	·0156	—	—	102·4	25	—	—	930	—	—	·5	999	25	—	
·148	·0312	1·0005	15·0	97·3	25	—	—	885	—	—	1·0	957	25	—	
·0475	·01	—	—	—	18	·0241	950[2]	1010	—	—	—	—	—	—	[3] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·142	·03	1·0004	15·0	—	18	—	878	932	—	—	·125	950[6]	20	—	
·237	·05	1·0013	15·0	—	18	—	841	894	—	—	·25	915	20	—	
·412	·087	1·0035	6·0	—	—	—	—	—	·678[4]	—	·5	848	20	—	
·473	·1	1·0035	15·0	—	18	—	794	844	—	—	1·0	741	20	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 383.
·773	·164	1·0065	15·0	—	—	—	—	—	·677	—	—	—	—	—	
2·327	·5	1·0197	15·0	—	18	·0226	665	706	—	—	—	—	—	—	[5] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 38.
4·31	·941	1·0366	14·4	—	—	—	—	—	·706	—	—	—	—	—	
4·57	1·0	1·0386	15·0	—	18	·0223	593	631	—	—	—	—	—	—	
12·81	3·0	1·1114	15·0	—	18	·0224	400	425	—	—	—	—	—	—	
20·12	5·0	1·1792	15·0	—	18	·0238	262	288	—	—	—	—	—	—	
21·53	5·41	1·1934	15·0	—	—	—	—	—	·779	—	—	—	—	—	
28·71	7·67	1·2685	5·6	—	—	—	—	—	·806	—	—	—	—	—	[6] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
—	10·0	—	—	—	18	·0340	62	66	—	—	—	—	—	—	
·0073	·00154	—	—	—	—	—	920[3]	978	—	—	—	—	—	—	
·0091	·00192	—	—	—	—	—	910	967	—	—	—	—	—	—	
·0153	·00322	—	—	—	—	—	900	975	—	—	—	—	—	—	

Zinc Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}ZnCl_2$, 67·82.

			°		°						°			°	
·000068	·00001	—	—	—	—	—	1036[1]	1101	—	—	—	—	—	—
·000136	·00002	—	—	—	—	—	1035	1100	—	—	—	—	—	—
·000407	·00006	—	—	—	—	—	1031	1096	—	—	—	—	—	—
·000678	·0001	—	—	—	—	—	1029	1094	—	—	—	—	—	—
·001356	·0002	—	—	—	—	—	1020	1084	—	—	—	—	—	—
·00407	·0006	—	—	—	—	—	1004	1067	—	—	—	—	—	—
·00678	·001	—	—	—	—	—	994	1057	—	—	1·0	777[4]	17·6	—
·01356	·002	—	—	—	—	—	979	1040	—	—	—	—	—	—
·0407	·006	—	—	—	—	—	939	998	—	—	—	—	—	—
·0678	·01	—	—	—	—	·0239	915	973	—	—	—	—	—	—
·2034	·03	1·0007	19·5	—	—	—	851	905	—	—	·125	1067[5]	25·0	—
·3	—	—	—	—	—	—	—	—	·7[3]	—	·25	1038	25·0	—
·337	·05	1·0023	19·5	—	—	—	817	868	—	—	·5	997	25·0	—
·672	·1	1·0062	19·5	—	—	—	768	816	—	—	1·0	919	25·0	—
3·28	·5	1·0312	19·5	—	—	—	601	639	—	—	—	—	—	—
6·4	1·0	1·0570	19·5	—	—	—	514	546	—	—	—	—	—	—
17·5	3·0	1·1600	19·5	—	—	—	280	298	—	—	—	—	—	—
26·52	—	—	—	—	—	—	—	—	1·08	—	—	—	—	—
26·88	5·0	1·2587	19·5	—	—	—	180	191	—	—	—	—	—	—
45·35	10·0	1·4921	19·5	—	—	—	60	64	—	—	—	—	—	—
·0117	·00173	—	—	—	—	—	910[2]	967	—	—	—	—	—	—
·023	·0034	—	—	—	—	—	870	924	—	—	—	—	—	—
2·5	·378	1·024	15·0	258[6]	18	·0213	682	725	—	—	—	—	—	—
5·0	·774	1·048	15·0	452	18	·0192	584	621	—	—	—	—	—	—
10·0	1·617	1·094	15·0	680	18	·0165	421	447	—	—	—	—	—	—
20·0	3·517	1·190	15·0	853	18	·0156	243	258	—	—	—	—	—	—
30·0	5·76	1·299	15·0	866	18	·0172	150	160	—	—	—	—	—	—
40·0	8·41	1·423	15·0	790	18	·0198	94	100	—	—	—	—	—	—
50·0	11·6	1·570	15·0	589	18	·0232	51	54	—	—	—	—	—	—
60·0	15·48	1·746	15·0	345	18	·0307	22	24	—	—	—	—	—	—

[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.

[2] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.

[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 397.

[4] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.

[5] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.

[6] Long, *Wied. Annal.* vol. xi. p. 37.

Cadmium Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}CdCl_2$, 91·37.

·0503	·0055	·9991	18·0	4·6[1]	18	·0231	835	887	—	—	—	—	—	—	[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 492.
·0999	·01095	·9996	18·0	8·34	18	·0226	761	809	—	—	—	—	—	—	
·20	·02194	1·0004	18·0	14·5	18	·0231	660	702	—	—	—	—	—	—	
·399	·0439	1·0022	18·0	24·7	18	·0227	563	598	—	—	—	—	—	—	
·518	·057	1·0045	10·5	—	—	—	—	—	·708[3]	—	—	—	—	—	
·599	·066	1·0039	18·0	33·8	18	·0224	512	544	—	—	—	—	—	—	[2] Grotian, *Wied. Annal.* vol. xviii. p. 194.
·769	·0849	1·0057	18·0	41·6	18	·0224	450	478	—	—	·125	1071[4]	25	—	
·997	·1102	1·0075	18·0	49·2	18	·0222	447	475	—	—	·25	1060	25	—	
1·0	·1105	1·0076	18·0	51·1	18	·0222	—	—	—	—	·5	1028	25	—	
1·002	·1100	—	—	—	—	—	—	—	·725	—	1·0	964	25	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 547.
·849	·0937	1·0062	18·0	45·5[2]	18	·0224	486	517	—	—	—	—	—	—	
5·01	·574	1·0437	18·0	155·0	18	·0218	270	287	—	—	—	—	—	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
10·04	1·203	1·0923	18·0	225·0	18	·0217	187	199	—	—	—	—	—	—	
14·79	—	—	—	—	—	—	—	—	·744	—	—	—	—	—	
14·94	1·874	1·1436	18·0	262·0	18	·0218	140	149	—	—	—	—	—	—	[5] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
19·8	2·603	1·1984	18·0	277·0	18	·0227	106	112	—	—	—	—	—	—	
22·96	3·12	1·2415	9·5	—	—	—	—	—	·772	—	—	—	—	—	
26·60	3·75	1·2891	9·5	—	—	—	—	—	·779	—	—	—	—	—	
29·97	4·373	1·3302	18·0	262·0	18	·0252	60	64	—	—	—	—	—	—	
33·53	5·10	1·3899	7·0	—	—	—	—	—	·873	—	—	—	—	—	
40·13	6·558	1·4899	18·0	204·0	18	·0291	31	33	—	—	—	—	—	—	
43·76	7·50	1·5657	6·8	—	—	—	—	—	1·014	—	—	—	—	—	
44·06	7·56	1·5681	9·8	—	—	—	—	—	1·016	—	—	—	—	—	
49·51	9·067	1·6697	18·0	131·0	18	·0353	14	15	—	—	—	—	—	—	
·00649	·00071	—	—	—	18	·0241	960[5]	1020	—	—	—	—	—	—	
·01097	·0012	—	—	—	18	·0244	920	978	—	—	—	—	—	—	
·0193	·00211	—	—	—	18	·0236	870	925	—	—	—	—	—	—	
·0471	·00515	—	—	—	18	·0237	780	829	—	—	—	—	—	—	

Cupric Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}CuCl_2$, 67·07.

·0063	·00094	—	—	—	18	—	930[1]	989	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·0107	·0016	—	—	—	18	—	900	957	—	—	·125	1064[2]	25	—	
·0201	·003	—	—	—	18	—	870	925	—	—	·25	1044	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 37.
·0396	·0059	—	—	—	18	—	860	915	—	—	·5	996	25	—	
·0885	·0132	—	—	—	18	—	750	797	—	—	1·0	907	25	—	

Ferrous Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}FeCl_2$, 63·32.

			°		°					°				°		
·0064	·00101	—	—	—	18	—	710[1]	754	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·01583	·0025	—	—	—	18	—	700	744	—	—	—	—	—	—	
·02406	·0038	—	—	—	18	—	680	723	—	—	—	—	—	—	

Nickel Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}NiCl_2$, 64·67.

·00789	·00122	—	—	—	18	·0245	730[1]	776	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·00963	·00149	—	—	—	18	·0240	730	776	—	—	·125	1070[2]	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 39.
·01196	·00185	—	—	—	18	—	740	787	—	—	·25	1046	25	—	
·01875	·0029	—	—	—	18	·0245	730	776	—	—	·5	996	25	—	
—	—	—	—	—	—	—	—	—	—	—	1·0	907	25	—	

Manganese Chloride.

Equivalent Gramme Molecule, $\frac{1}{2}MnCl_2$, 62·87.

·522	·083	1·0045	9·0	—	—	—	—	—	·682[2]	—	—	—	—	—	[1] Long, *Wied. Annal.* vol. xi. p. 37.
5·0	·831	1·0456	15·0	492[1]	18	·0216	592	629	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 383.
10·0	1·733	1·0895	15·0	790	18	·0206	456	485	—	—	·125	1068[3]	25	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 37.
15·0	2·715	1·1378	15·0	987	18	·0202	363	386	—	—	·25	1043	25	—	
20·0	3·785	1·1900	15·0	1061	18	·0206	280	298	—	—	·5	995	25	—	
23·22	4·524	1·2275	6·6	—	—	—	—	—	·758	—	1·0	904	25	—	
25·0	4·960	1·2472	15·0	1020	18	·0203	206	219	—	—	—	—	—	—	
28·0	5·710	1·2828	15·0	950	18	·0208	166	176	—	—	—	—	—	—	

Aluminium Chloride.

Equivalent Gramme Molecule, $\frac{1}{6}Al_2Cl_6$, 44·37.

·00697	·00157	—	—	—	18	—	830[1]	882	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·00887	·002	—	—	—	18	—	800	850	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 391.
·01642	·0037	—	—	—	18	—	806	857	—	—	—	—	—	—	
4·22	—	—	—	—	—	—	—	—	·714[2]	—	—	—	—	—	

Ferric Chloride.

Equivalent Gramme Molecule, $\frac{1}{6}Fe_2Cl_6$, 54.

·0054	·0010	—	—	—	18	—	2360[1]	2509	—	—	—	—	—	—
·0108	·0020	—	—	—	18	—	1660	1765	—	—	—	—	—	—
·0130	·0024	—	—	—	18	—	1510	1605	—	—	—	—	—	—
·0184	·0034	—	—	—	18	—	1460	1552	—	—	—	—	—	—
·0286	·0053	—	—	—	18	—	1290	1371	—	—	—	—	—	—
·0324	·0060	—	—	—	18	—	1300	1382	—	—	—	—	—	—
·0168	·00312	—	—	—	18	—	—	1617[2]	—	—	—	—	—	—
·0337	·00625	—	—	—	18	—	—	1496	—	—	—	—	—	—
·0674	·0125	—	—	—	18	—	—	1356	—	—	—	—	—	—
·1348	·025	—	—	—	18	—	—	1211	—	—	—	—	—	—
·2696	·05	—	—	—	18	—	—	1053	—	—	—	—	—	—
·539	·1	—	—	—	18	—	—	908	—	—	—	—	—	—
1·078	·2	—	—	—	18	—	—	741	—	—	—	—	—	—
3·81	—	—	—	—	—	—	—	—	·6[3]	—	—	—	—	—
32·51	—	—	—	—	—	—	—	—	·746	—	—	—	—	—

[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx.

[2] Fitzpatrick, *Phil. Mag.* vol. xxiv. p. 377.

[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 389.

Hydrobromic Acid.

Equivalent Gramme Molecule, HBr, 80·75.

·00195	·000244	—	—	87·8[1]	25	—	—	3559	—	—	—	—	—	—
·0039	·000488	—	—	88·9	25	—	—	3612	—	—	—	—	—	—
·0078	·000976	—	—	89·7	25	—	—	3636	—	—	—	—	—	—
·0156	·00195	—	—	89·8	25	—	—	3644	—	—	—	—	—	—
·0312	·0039	—	—	89·6	25	—	—	3640	—	—	—	—	—	—
·0625	·0078	—	—	89·4	25	—	—	3632	—	—	—	—	—	—
·125	·0156	—	—	88·9	25	—	—	3612	—	—	—	—	—	—
·25	·0312	—	—	87·9	25	—	—	3571	—	—	—	—	—	—
·502	·0625	1·004	14	86·6	25	—	—	3519	—	—	—	—	—	—
1·0	·125	1·007	14	85·1	25	—	—	3458	—	—	—	—	—	—
2·0	·25	1·014	14	83·4	25	—	—	3389	—	—	—	—	—	—
3·92	·5	1·027	14	80·4	25	·0153	—	3267	—	—	—	—	—	—
10·36	—	—	—	—	—	—	—	—	·178[2]	—	—	—	—	—

[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 438.

[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 399.

Potassium Bromide.

Equivalent Gramme Molecule, KBr, 118·79.

			°		°					°			°		
·851	·072	1·0063	7·0	—	—	—	—	—	·514[2]	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
—	·5	—	—	497[1]	18	·0205	994	1057	—	—	—	—	—	—	
—	1·0	—	—	960	18	·0193	960	1020	—	—	1·309	1013[3]	20	·0217	
—	1·5	—	—	1404	18	·0184	936	995	—	—	2·321	1028	20	·0203	
—	2·0	—	—	1832	18	·0177	916	974	—	—	3·824	999	20	·0179	[2] Hittorf, *Pogg. Annal.* vol. xcviii. p. 27.
—	2·5	—	—	2243	18	·0171	897	954	—	—	—	—	—	—	
—	3·0	—	—	2623	18	·0166	874	929	—	—	—	—	—	—	
29·7	3·15	1·261	12·2	—	—	—	—	—	·528	—	—	—	—	—	[3] Sprung, *Pogg. Annal.* vol. clix. p. 11.
—	3·5	—	—	2977	18	·0160	850	904	—	—	—	—	—	—	
—	4·0	—	—	3294	18	·0156	824	876	—	—	—	—	—	—	

Cadmium Bromide.

Equivalent Gramme Molecule, $\frac{1}{2}CdBr_2$, 135·75.

·0324	·002386	·9990	18	2·15[1]	18	·0235	899	956	—	—	—	—	—	—	[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 493.
·0748	·005517	·99935	18	4·37	18	·0237	792	842	—	—	—	—	—	—	
·154	·01134	1·00002	18	7·84	18	·0239	691	735	—	—	—	—	—	—	
·253	·01867	1·0010	18	11·6	18	·0237	623	662	—	—	—	—	—	—	
·506	·03743	1·0031	18	19·8	18	·0238	529	562	—	—	—	—	—	—	
1·013	·07517	1·0075	18	33·3	18	·0233	443	471	—	—	—	—	—	—	[2] Grotian, *Wied. Annal.* vol. xviii. p. 194.
1·01	·0751	1·0073	18	33·4[2]	18	·0232	445	473	—	—	—	—	—	—	
5·07	·390	1·0437	18	101·0	18	·0225	259	275	—	—	—	—	—	—	
10·10	·813	1·0916	18	152·0	18	·0232	187	199	—	—	—	—	—	—	
20·11	1·781	1·2004	18	219·0	18	·0239	123	131	—	—	—	—	—	—	
29·95	2·936	1·3288	18	253·0	18	·0258	86	91·4	—	—	—	—	—	—	
42·99	4·904	1·5464	18	242·0	18	·0288	49	52	—	—	—	—	—	—	

Hydriodic Acid.

Equivalent Gramme Molecule, HI, 127·53.

·0031	·000244	—	—	87·81[1]	25	—	—	3567	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 438.
·0062	·000488	—	—	89·0	25	—	—	3616	—	—	—	—	—	—	
·0123	·000976	—	—	89·3	25	—	—	3628	—	—	—	—	—	—	
·0247	·00195	—	—	89·7	25	—	—	3644	—	—	—	—	—	—	
·0495	·0039	—	—	89·7	25	—	—	3644	—	—	—	—	—	—	

·099	·0078	—	—	89·4	25	—	—	3632	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 401.
·198	·0156	—	—	88·7	25	—	—	3608	—	—	—	—	—	—	
·397	·0312	—	—	87·6	25	—	—	3559	—	—	—	—	—	—	
·792	·0625	1·0058	13·5	86·4	25	—	—	3511	—	—	—	—	—	—	
·844	—	—	—	—	25	—	—	—	·258[2]	—	—	—	—	—	
1·576	·125	1·0117	13·5	84·9	25	·0158	—	3480	—	—	—	—	—	—	
3·11	·25	1·0230	13·5	83·2	25	—	—	3381	—	—	—	—	—	—	
6·1	·5	1·0453	13·5	80·4	25	—	—	3267	—	—	—	—	—	—	
17·17	—	—	—	—	—	—	—	—	·201	—	—	—	—	—	

Potassium Iodide.

Equivalent Gramme Molecule, KI, 165·9.

·017	·000976	—	—	143·1[1]	25	—	—	1319	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·034	·00195	—	—	139·1	25	—	—	1282	—	—	—	—	—	—	
·067	·0039	—	—	136·1	25	—	—	1254	—	—	—	—	—	—	
·134	·0078	—	—	132·9	25	—	—	1225	—	—	—	—	—	—	
·269	·0156	—	—	129·3	25	—	—	1192	—	—	—	—	—	—	[2] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·518	·0312	—	—	125·4	25	—	—	1156	—	—	—	—	—	—	
·000166	·00001	—	—	—	18	—	1207[2]	1283	—	—	—	—	—	—	
·000332	·00002	—	—	—	18	—	1216	1293	—	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. xcviii. p. 29.
·000995	·00006	—	—	—	18	—	1216	1293	—	—	—	—	—	—	
·00166	·0001	—	—	—	18	—	1216	1293	—	—	—	—	—	—	
·00332	·0002	—	—	—	18	—	1214	1291	—	—	—	—	—	—	
·00996	·0006	—	—	—	18	—	1209	1285	—	—	·541	1009[4]	20	·0242	[4] Sprung, *Pogg. Annal.* vol. clix. p. 1.
·0166	·001	—	—	—	18	—	1203	1279	—	—	1·171	1057	20	·0219	
·0332	·002	—	—	—	18	—	1197	1273	—	—	2·610	1082	20	·0190	[5] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·0996	·006	—	—	—	18	—	1176	1250	—	—	4·119	1046	20	·0170	
·166	·01	—	—	—	18	·0219	1161	1234	—	—	5·257	986	20	·0158	
·495	·03	—	—	—	18	—	1123	1194	—	—	—	—	—	—	
·8255	·05	1·0048	19·5	—	18	—	1102	1172	—	—	—	—	—	—	
1·640	·1	1·0112	19·5	—	18	—	1069	1136	—	—	1·0	1066[5]	20	—	
7·823	·5	1·0603	19·5	—	18	·0203	997	1060	—	—	—	—	—	—	
10·57	·705	1·1081	12·0	—	—	—	—	—	·511[3]	—	—	—	—	—	
14·84	1·0	1·1180	19·5	—	18	·0194	968	1029	—	—	—	—	—	—	
26·86	2·01	1·2414	11·0	—	—	—	—	—	·512	—	—	—	—	—	
36·8	3·0	1·3530	19·5	—	18	·0156	900	957	—	—	—	—	—	—	
52·3	5·0	1·5860	19·5	—	18	·0142	770	819	—	—	—	—	—	—	

Ammonium Iodide.

Equivalent Gramme Molecule, NH_4I, 144·84.

			°		°				°			°			
10·0	·735	1·0652	18	722[1]	18	·0202	982	1044	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
20·0	1·574	1·1397	18	1494	18	·0193	949	1009	—	—	—	—	—	—	
30·0	2·54	1·2260	18	2318	18	·0180	912	969	—	—	—	—	—	—	
40·0	3·663	1·3260	18	3166	18	·0167	867	922	—	—	—	—	—	—	
50·0	4·98	1·4415	18	3917	18	·0154	786	835	—	—	—	—	—	—	

Sodium Iodide.

Equivalent Gramme Molecule, NaI, 149·84.

5·0	·346	1·0374	18	279[1]	18	·0222	806	857	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
10·0	·721	1·0803	18	543	18	·0216	753	801	—	—	—	—	—	—	
20·0	1·567	1·1735	18	1069	18	·0204	682	725	—	—	—	—	—	—	
30·0	2·57	1·2836	18	1545	18	·0198	600	638	—	—	—	—	—	—	
40·0	3·77	1·4127	18	1972	18	·0199	523	556	—	—	—	—	—	—	

Lithium Iodide.

Equivalent Gramme Molecule, LiI, 133·82.

5·0	·387	1·0361	18	277[1]	18	·0219	716	761	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
10·0	·804	1·0756	18	536	18	·0216	666	708	—	—	—	—	—	—	
15·0	1·253	1·1180	18	783	18	·0212	625	665	—	—	—	—	—	—	
20·0	1·740	1·1643	18	1023	18	·0207	588	625	—	—	—	—	—	—	
25·0	2·267	1·2138	18	1258	18	·0203	555	590	—	—	—	—	—	—	

Cadmium Iodide.

Equivalent Gramme Molecule, $\frac{1}{2}CdI_2$, 182·53.

·0429	·00235	·9991	18·0	1·95[1]	18	·0257	829	881	—	—	—	—	—	—	[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 493.
·1	·0055	·9996	18·0	3·83	18	·0261	696	740	—	—	—	—	—	—	
·204	·0112	1·0005	18·0	6·6	18	·0262	589	626	—	—	—	—	—	—	
·399	·0220	1·0021	18·0	10·7	18	·0264	486	517	—	—	—	—	—	—	
·6	·0330	1·0038	18·0	14·1	18	·0266	427	454	·613[3]	—	—	—	—	—	[2] Grotian, *Wied. Annal.* vol. xviii. p. 194.
·8	·0441	1·0056	18·0	17·0	18	·0270	386	410	—	—	—	—	—	—	
1·0	·0552	1·0072	18·0	19·7	18	·0271	356	378	—	—	—	—	—	—	
1·017	·0562	1·0073	18·0	19·7[2]	18	·0286	350	372	—	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 543.
1·41	—	—	—	—	—	—	—	—	·642	—	—	—	—	—	

4·87	·278	1·0413	18·0	55·5	18	·0261	200	213	—	—	—	—	—	—	
5·23	·3	1·0456	11·2	—	—	—	—	—	·931	—	—	—	—	—	
10·03	·599	1·0885	18·0	96·6	18	·0248	161	171	—	—	—	—	—	—	
14·67	·913	1·1354	18·0	132·0	18	·0242	144	153	—	—	—	—	—	—	
19·0	1·230	1·1854	11·8	—	—	—	—	—	1·14	—	—	—	—	—	
19·54	1·274	1·1890	18·0	169·0	18	·0240	132	140	—	—	—	—	—	—	
24·75	1·700	1·2551	11·0	—	—	—	—	—	1·192	—	—	—	—	—	
29·6	2·138	1·3171	18·0	234·0	18	·0244	101	107	—	—	—	—	—	—	
35·32	—	—	—	—	—	—	—	—	1·258	—	—	—	—	—	
40·03	3·254	1·4821	18·0	281·0	18	·0254	86	91	—	—	—	—	—	—	
44·13	3·770	1·5576	18·0	290·0	18	·0258	77	82	—	—	—	—	—	—	
47·5	—	—	18·0	293·0	18	·0263	—	—	—	—	—	—	—	—	

Potassium Cadmium Iodide.

Equivalent Gramme Molecule, $\frac{1}{2}K_2CdI_4$, 347·43.

·0328	·00094	·99895	18	1·9[1]	18	·0226	2016	2143	—	—	—	—	—	—	
·0596	·00171	·99921	18	3·32	18	·0231	1935	2057	—	—	—	—	—	—	
·0804	·00231	·99938	18	4·32	18	·0228	1869	1987	—	—	—	—	—	—	
·10	·00287	·99945	18	5·26	18	·0229	1831	1946	—	—	—	—	—	—	
·25	·00719	1·0007	18	11·8	18	·0233	1645	1748	—	—	—	—	—	—	
·50	·01441	1·0027	18	21·6	18	·0231	1498	1592	—	—	—	—	—	—	
1·003	·02923	1·0067	18	38·5	18	·0234	1317	1400	—	—	—	—	—	—	
1·674	—	—	—	—	—	—	—	—	·563	—	—	—	—	—	
1·006	·0291	1·0065	18	38·32	18	·0235	1309	1391	—	—	—	—	—	—	
5·04	·151	1·0387	18	148·0	18	·0227	980	1042	—	—	—	—	—	—	
10·14	·315	1·0821	18	278·0	18	·0224	882	938	—	—	—	—	—	—	
15·11	·490	1·1280	18	408·0	18	·0218	833	885	—	—	—	—	—	—	
25·25	·896	1·2338	18	689·0	18	·0214	769	817	—	—	—	—	—	—	
30·33	—	—	—	—	—	—	—	—	·79	—	—	—	—	—	
34·96	1·362	1·3552	18	986·0	18	·0207	724	770	—	—	—	—	—	—	
45·12	1·957	1·5086	18	1319·0	18	·0198	674	716	—	—	—	—	—	—	

Hydrofluoric Acid.

Equivalent Gramme Molecule, HF, 20·1.

·000488	·000244	—	—	69·42[1]	25	—	—	3134[2]	—	—	—	—	—	—	
·000976	·000488	—	—	59·56	25	—	—	2689	—	—	—	—	—	—	
·00195	·000976	—	—	49·49	25	—	—	2235	—	—	—	—	—	—	
·0039	·00195	—	—	39·11	25	—	—	1765	—	—	—	—	—	—	

[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 493.

[2] Grotian, *Wied. Annal.* vol. xviii. p. 194.

[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 527.

[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 303.

[2] At 25°.

Hydrofluoric Acid—*continued.*

Equivalent Gramme Molecule, HF, 20·1.

			°		°					°				°	
·0078	·0039	—	—	30·30	25	—	—	1368	—	—	—	—	—	—	
·0156	·0078	—	—	23·11	25	—	—	1043	—	—	—	—	—	—	
·0312	·0156	—	—	17·38	25	—	—	786	—	—	—	—	—	—	
·0625	·0312	—	—	13·14	25	—	—	594	—	—	—	—	—	—	
·125	·0625	—	—	10·00	25	—	—	451	—	—	—	—	—	—	
·25	·125	—	—	7·89	25	—	—	356	—	—	—	—	—	—	
·5	·25	—	—	6·54	25	—	—	296	—	—	—	—	—	—	

Potassium Fluoride.

Equivalent Gramme Molecule, KF, 58·14.

—	·5	—	—	367[1]	18	—	734	780	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
—	1·0	—	—	676	18	·0214	676	718	—	—	—	—	—	—	
—	2·0	—	—	1196	18	·0217	598	636	—	—	—	—	—	—	
—	3·0	—	—	1609	18	·0219	536	570	—	—	—	—	—	—	
—	4·0	—	—	1936	18	·0220	484	514	—	—	—	—	—	—	
—	5.0	—	—	2182	18	·0222	436	463	—	—	—	—	—	—	
—	6·0	—	—	2338	18	·0226	390	414	—	—	—	—	—	—	
—	7·0	—	—	2416	18	·0232	345	366	—	—	—	—	—	—	
—	8·0	—	—	2422	18	·0238	303	322	—	—	—	—	—	—	
—	9·0	—	—	2385	18	·0248	265	282	—	—	—	—	—	—	
—	10·0	—	—	2303	18	·0260	230	244	—	—	—	—	—	—	

Nitric Acid.

Equivalent Gramme Molecule, HNO_3, 63·04.

·000063	·00001	—	—	—	18	—	1144[1]	1213	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000126	·00002	—	—	—	18	—	1904	2024	—	—	—	—	—	—	
·00038	·00006	—	—	—	18	—	2863	3043	—	—	—	—	—	—	
·00063	·0001	—	—	—	18	—	3088	3282	—	—	—	—	—	—	
·00126	·0002	—	—	—	18	—	3285	3492	—	—	—	—	—	—	
·00378	·0006	—	—	—	18	—	3408	3622	—	—	—	—	—	—	
·0063	·001	—	—	—	18	—	3427	3643	—	—	—	—	—	—	
·0126	·002	—	—	—	18	—	3448	3665	—	—	—	—	—	—	
·0378	·006	—	—	—	18	—	3421	3636	—	—	—	—	—	—	
·063	·01	—	—	—	18	·0162	3395	3609	—	—	—	—	—	—	

·189	·03	—	—	—	18	—	3328	3537	—	—	1·02	950[2]	20	·0227	[2] Grotian, *Pogg. Annal.* vol. clx. p. 262.
·315	·05	—	—	—	18	—	3289	3497	—	—	2·11	921	20	·0211	
·63	·1	1·0034	15	—	18	—	3225	3428	—	—	3·28	874	20	·0200	
3·09	·5	1·0185	15	—	18	—	2991	3179	—	—	5·865	788	20	·0184	[3] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 439.
6·09	1·0	1·0354	15	—	18	—	2770	2944	—	—	7·24	669	20	·0181	
17·17	3·0	1·1010	15	—	18	—	2070	2200	—	—	—	—	—	—	
22·0	5·0	1·1660	15	—	18	—	1470	1562	—	—	—	—	—	—	
48·26	10·0	1·3061	15	—	18	—	610	648	—	—	—	—	—	—	[4] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·00075	·000121	—	—	83·9[3]	25	—	—	3234	—	—	—	—	—	—	
·0015	·000243	—	—	86·7	25	—	—	3432	—	—	—	—	—	—	
·0030	·000487	—	—	88·2	25	—	—	3537	—	—	—	—	—	—	
·0061	·000975	—	—	89·0	25	—	—	3585	—	—	—	—	—	—	
·0122	·00195	—	—	88·9	25	—	—	3591	—	—	—	—	—	—	
·0245	·0039	—	—	88·5	25	—	—	3580	—	—	—	—	—	—	
·049	·0078	—	—	88·4	25	—	—	3574	—	—	—	—	—	—	
·098	·0156	—	—	87·5	25	—	—	3544	—	—	—	—	—	—	
·197	·0312	—	—	86·2	25	—	—	3500	—	—	—	—	—	—	
·393	·0625	1·0017	15	84·9	25	—	—	3443	—	—	—	—	—	—	
·784	·125	1·0044	15	82·7	25	—	—	3358	—	—	—	—	—	—	
1·56	·25	1·0090	15	80·2	25	—	—	3261	—	—	—	—	—	—	
3·09	·5	1·0185	15	77·9	25	—	—	3159	—	—	—	—	—	—	
·396	·063	1·0019	15	20·5[4]	18	—	3254	3459	—	—	—	—	—	—	
·785	·126	1·0046	15	40·3	18	—	3200	3401	—	—	—	—	—	—	
1·57	·252	1·0094	15	78·3	18	—	3103	3298	—	—	—	—	—	—	
3·12	·504	1·0188	15	150·0	18	—	2953	3139	—	—	—	—	—	—	

Potassium Nitrate.

Equivalent Gramme Molecule, KNO_3, 101·17.

·000101	·00001	—	—	—	18	—	1215[1]	1292	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000202	·00002	—	—	—	18	—	1198	1274	—	—	—	—	—	—	
·000607	·00006	—	—	—	18	—	1220	1297	—	—	—	—	—	—	
·00101	·0001	—	—	—	18	—	1207	1283	—	—	·649	993[2]	20	·0246	[2] Sprung, *Pogg. Annal.* vol. clix. p. 12.
·00202	·0002	—	—	—	18	—	1199	1275	—	—	1·3	1008	20	·0225	
·00607	·0006	—	—	—	18	—	1190	1265	—	—	1·943	988	20	·0214	[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·0101	·001	—	—	—	18	—	1180	1255	—	—	—	—	—	—	
·0202	·002	—	—	—	18	—	1173	1247	—	—	1·0	1018[3]	20	—	
·0607	·006	—	—	—	18	—	1140	1212	—	—	—	—	—	—	

Potassium Nitrate—*continued.*

Equivalent Gramme Molecule, KNO_3, 101·17.

			°		°				°				°		
·101	·01	·99988	15·0	—	18	·0216	1122	1193	—	—	·125	981[6]	20	—	[4] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·303	·03	1·0013	15·0	—	18	—	1067	1134	—	—	·25	986	20	—	
·504	·05	1·0028	15·0	—	18	—	1037	1102	—	—	·5	991	20	—	
1·005	·1	1·0064	15·0	—	18	—	983	1045	—	—	1·0	1003	20	—	[5] Hittorf, *Pogg. Annal.* vol. ciii. p. 41.
1·06	·105	1·0068	8·0	—	—	—	—	—	·497[5]	—	—	—	—	—	
3·08	·31	1·0201	7·0	—	—	—	—	—	·494	—	—	—	—	—	
4·9	·5	1·0314	15·0	—	18	·0209	839	892	—	—	·125	987[7]	20	—	[6] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 37.
9·4	·99	1·0620	11·4	—	—	—	—	—	·487	—	·25	987	20	—	
9·52	1·0	1·0621	15·0	—	18	·0206	752	799	—	—	·5	989	20	—	
17·8	2·1	1·1290	12·0	—	—	—	—	—	·479	—	1·0	994	20	—	
—	3·0	—	—	—	18	·0188	572	608	—	—	—	—	—	—	[7] Mutzel, *Wied. Annal.* vol. xliii. p. 26.
·0099	·000976	—	—	135·9[4]	25	—	—	1255	—	—	—	—	—	—	
·0197	·00195	—	—	132·6	25	—	—	1224	—	—	—	—	—	—	
·0395	·0039	—	—	129·2	25	—	—	1193	—	—	—	—	—	—	[8] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·079	·0078	—	—	125·7	25	—	—	1161	—	—	—	—	—	—	
·158	·0156	—	—	121·6	25	—	—	1123	—	—	—	—	—	—	
·316	·0312	—	—	117·2	25	—	—	1086	—	—	—	—	—	—	
·63	·0625	1·0037	15·0	61·9[8]	18	—	991	1053	—	—	—	—	—	—	
1·254	·125	1·0080	15·0	117·8	18	—	942	1001	—	—	—	—	—	—	
2·49	·25	1·0159	15·0	221·0	18	—	882	937	—	—	—	—	—	—	
4·9	·5	1·0314	15·0	408·0	18	—	816	867	—	—	—	—	—	—	

Ammonium Nitrate.

Equivalent Gramme Molecule, NH_4NO_3, 79·9.

—	·5	—	—	442·0[1]	18	·0206	884	939	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
—	1·0	—	—	831·0	18	·0199	831	883	—	—	·767[2]	1011	20	·0236	
—	2·0	—	—	1507·0	18	·0187	754	801	—	—	1·606	1018	20	·0223	
—	3·0	—	—	2082·0	18	·0178	694	737	—	—	3·8	1000	20	·0167	
—	4·0	—	—	2561·0	18	·0170	640	680	—	—	5·46	927	20	·0169	[2] Sprung, *Pogg. Annal.* vol. clix. p. 10.
—	5·0	—	—	2929·0	18	·0165	586	623	—	—	7·71	743	20	·0173	
—	6·0	—	—	3190·0	18	·0161	532	565	—	—	—	—	—	—	
—	7·0	—	—	3351·0	18	·0158	479	505	—	—	—	—	—	—	
—	8·0	—	—	3419·0	18	·0157	427	454	—	—	—	—	—	—	

—	·0625	—	—	62·9[3]	18	—	1006	1069	—	—	—	—	—	—	[3] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	·125	—	—	120·1	18	—	961	1021	—	—	—	—	—	—	
—	·25	—	—	227·0	18	—	908	965	—	—	—	—	—	—	
—	·5	—	—	432·7	18	—	865	919	—	—	—	—	—	—	

Sodium Nitrate.

Equivalent Gramme Molecule, $NaNO_3$, 85·08.

·000085	·00001	—	—	—	18	—	975[1]	1036	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·00017	·00002	—	—	—	18	—	972	1033	—	—	—	—	—	—	
·00051	·00006	—	—	—	18	—	970	1031	—	—	·895	931[5]	20	·0240	
·00085	·0001	—	—	—	18	—	975	1036	—	—	1·58	872	20	·0241	
·0017	·0002	—	—	—	18	—	966	1027	—	—	2·422	801	20	·0234	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·0051	·0006	—	—	—	18	—	956	1016	—	—	4·614	583	20	·0245	
·0085	·001	—	—	—	18	—	952	1013	—	—	—	—	—	—	
·017	·002	—	—	—	18	—	942	1001	—	—	1·0	929[6]	20	—	
·051	·006	—	—	—	18	—	921	979	—	—	—	—	—	—	[3] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 80.
·085	·01	—	—	—	18	·0226	907	964	—	—	·125	978[7]	20	—	
·255	·03	1·0004	20·2	—	18	—	877	932	—	—	·25	968	20	—	
·424	·05	1·0018	20·2	—	18	—	855	909	—	—	·5	945	20	—	
·77	·091	1·0052	13·0	—	—	—	—	—	·613[4]	—	1·0	893	20	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 377.
·846	·1	1·0053	20·2	—	18	—	817	868	—	—	—	—	—	—	
1·057	·125	1·0074	10·0	—	—	—	—	—	·615	—	—	—	—	—	
1·72	·204	1·0118	12·0	—	—	—	—	—	·613	—	—	—	—	—	[5] Sprung, *Pogg. Annal.* vol. clix. p. 14.
2·8	·335	1·0195	12·0	—	—	—	—	—	·614	—	—	—	—	—	
4·14	·5	1·0273	20·2	—	18	·0223	694	738	—	—	—	—	—	—	
8·07	1·0	1·0542	20·2	—	18	·0219	617	656	—	—	—	—	—	—	[6] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
22·04	3·0	1·1581	20·2	—	18	·0216	430	457	—	—	—	—	—	—	
25·0	3·5	1·1904	9·2	—	—	—	—	—	·600	—	—	—	—	—	
·53	·0625	1·0026	20·2	52·1[2]	18	—	834	886	—	—	—	—	—	—	[7] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
1·056	·125	1·0067	20·2	98·4	18	—	787	836	—	—	—	—	—	—	
2·1	·25	1·0137	20·2	184·8	18	—	739	785	—	—	—	—	—	—	
4·14	·5	1·0273	20·2	340·0	18	—	680	725	—	—	—	—	—	—	
·0083	·000976	—	—	113·7[3]	25	—	—	1043	—	—	—	—	—	—	
·0166	·00195	—	—	111·2	25	—	—	1020	—	—	—	—	—	—	
·0331	·0039	—	—	108·5	25	—	—	996	—	—	—	—	—	—	
·0662	·0078	—	—	105·6	25	—	—	969	—	—	—	—	—	—	
·1325	·0156	—	—	102·4	25	—	—	940	—	—	—	—	—	—	
·265	·0312	1·0004	20·2	99·0	25	—	—	909	—	—	—	—	—	—	

Lithium Nitrate.

Equivalent Gramme Molecule, $LiNO_3$, 68·9.

			°		°				°				°		
·0067	·000976	—	—	105·1[1]	25	—	—	962	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 83.
·0134	·00195	—	—	102·0	25	—	—	934	—	—	—	—	—	—	
·0268	·0039	—	—	99·0	25	—	—	906	—	—	—	—	—	—	
·0535	·0078	—	—	96·1	25	—	—	880	—	—	—	—	—	—	
·107	·0156	—	—	92·6	25	—	—	848	—	—	—	—	—	—	
·214	·0312	—	—	89·6	25	—	—	820	—	—	—	—	—	—	[2] Fitzpatrick, *Phil. Mag.* (5th series), vol. xxiv. p. 377.
·0134	·00195	—	—	1·65[2]	18	—	844	900	—	—	—	—	—	—	
·0268	·0039	—	—	3·26	18	—	839	889	—	—	—	—	—	—	
·0535	·0078	—	—	6·45	18	—	825	880	—	—	—	—	—	—	
·107	·0156	—	—	12·6	18	—	810	856	—	—	—	—	—	—	
·214	·0312	—	—	24·2	18	—	774	827	—	—	—	—	—	—	
·428	·0625	—	—	46·5	18	—	744	790	—	—	—	—	—	—	
—	·125	—	—	88·5	18	—	708	752	—	—	—	—	—	—	
—	·25	—	—	166·0	18	—	664	707	—	—	—	—	—	—	
—	·5	—	—	303·0	18	—	606	645	—	—	—	—	—	—	
—	1·0	—	—	532·0	18	—	532	550	—	—	—	—	—	—	

Silver Nitrate.

Equivalent Gramme Molecule, $AgNO_3$, 169·9.

·00017	·00001	—	—	—	18	—	1080[1]	1148	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·00034	·00002	—	—	—	18	—	1073	1141	—	—	—	—	—	—	
·00102	·00006	—	—	—	18	—	1077	1145	—	—	—	—	—	—	
·0017	·0001	—	—	—	18	—	1078	1146	—	—	—	—	—	—	
·0034	·0002	—	—	—	18	—	1077	1145	—	—	—	—	—	—	
·0102	·0006	—	—	—	18	—	1069	1136	—	—	—	—	—	—	
·017	·001	—	—	—	18	—	1068	1135	—	—	·125	1093[3]	25	—	[2] Hittorf, *Pogg. Annal.* vol. lxxxix. p. 203.
·034	·002	—	—	—	18	—	1057	1124	—	—	·25	1086	25	—	
·102	·006	—	—	—	18	—	1033	1098	—	—	·5	1071	25	—	
·17	·01	—	—	—	18	·0221	1017	1081	—	—	1·0	1033	25	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.
·403	—	1·0044	9·6	—	—	—	—	—	·524[2]	9·6	—	—	—	—	
·507	·03	—	—	—	18	—	966	1027	—	—	—	—	—	—	
·842	·05	1·0070	18·0	—	18	—	936	995	—	—	—	—	—	—	
·947	—	1·0076	18·6	—	—	—	—	—	·526	18·6	—	—	—	—	
1·657	·1	1·0131	18·0	—	18	—	886	942	—	—	—	—	—	—	
1·98	—	1·0166	18·5	—	—	—	—	—	·526	18·5	—	—	—	—	
4·06	—	1·0343	18·4	—	—	—	—	—	·527	18·4	—	—	—	—	

6·45	—	1·0558	19·2	—	—	—	—	—	·525	19·2	—	—	—	—	[4] Loeb and Nernst, *Zeitschrift für physik. Chemie*, vol. ii. p. 956.
7·927	·5	1·0693	18·0	—	18	·0218	728	774	—	—	—	—	—	—	
8·772	—	1·0774	18·8	—	—	—	—	—	·510	18·8	—	—	—	—	
14·91	1·0	1·1395	18·0	—	18	·0216	635	675	—	—	—	—	—	—	
16·18	—	1·1534	18·4	—	—	—	—	—	·495	18·4	—	—	—	—	[5] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
26·81	—	1·2788	19·2	—	—	—	—	—	·478	19·0	—	—	—	—	
28·73	—	1·3079	11·1	—	—	—	—	—	·468	11·2	—	—	—	—	
36·11	3·0	1·4120	18·0	—	18	·0207	448	476	—	—	—	—	—	—	
50·44	5·0	1·6843	18·0	—	18	·0206	351	373	—	—	—	—	—	—	
·0136	·0008	—	—	1232[4]	25	—	—	1134	—	—	—	—	—	—	
·0255	·0015	—	—	1221	25	—	—	1124	—	—	—	—	—	—	
·051	·003	—	—	1206	25	—	—	1110	—	—	—	—	—	—	
·119	·007	—	—	1188	25	·0222	—	1094	—	—	—	—	—	—	
·178	·0105	—	—	—	—	—	—	—	·524[4]	26·0	—	—	—	—	
·255	·015	—	—	1153	25	—	—	1061	—	—	—	—	—	—	
·42	·025	—	—	1126	25	·0217	—	1037 {	·522	26·0	—	—	—	—	
									·538	0·0	—	—	—	—	
·842	·05	1·007	18·0	1086	25	—	—	1000	—	—	—	—	—	—	
—	·052	—	—	—	—	—	—	—	·524	26·0	—	—	—	—	
1·657	·1	1·0131	18·0	1022	25	·0213	—	941	—	—	—	—	—	—	
—	·104	—	—	—	—	—	—	—	·528	20·0	—	—	—	—	
·00763	·00045	—	—	—	18	·0228	1040[5]	1105	—	—	—	—	—	—	
·00915	·00054	—	—	—	18	·0229	1030	1095	—	—	—	—	—	—	
·0166	·00097	—	—	—	18	·0227	1010	1074	—	—	—	—	—	—	
·0410	·00242	—	—	—	18	—	990	1052	—	—	—	—	—	—	

STRONTIUM NITRATE.

Equivalent Gramme Molecule, $\frac{1}{2}Sr(NO_3)_2$, 105·54.

5·0	·494	1·0418	15	289[1]	18	·0225	585	622	—	—	·125	1080[3]	25	—	[1] Long, *Wied. Annal.* vol. xi. p. 37.
10·0	1·029	1·0857	15	493	18	·0225	479	509	—	—	·25	1067	25	—	
15·0	1·608	1·1318	15	645	18	·0227	401	426	—	—	·5	1042	25	—	[2] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
20·0	2·240	1·1815	15	750	18	·0228	335	356	—	—	1·0	980	25	—	
25·0	2·929	1·2363	15	810	18	·0226	277	294	—	—	—	—	—	—	
35·0	4·490	1·3542	15	805	18	·0241	179	190	—	—	—	—	—	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.
·00918	·00087	—	—	—	18	—	980[2]	1042	—	—	·125	961[4]	20	—	
·01076	·00102	—	—	—	18	—	990	1052	—	—	·25	931	20	—	
·01604	·00152	—	—	—	18	—	950	1010	—	—	·5	878	20	—	[4] Mutzel, *Wied. Annal.* vol. xliii. p. 21.
·03747	·00355	—	—	—	18	—	920	978	—	—	1·0	777	20	—	

Barium Nitrate.

Equivalent Gramme Molecule, $\frac{1}{2}Ba(NO_3)_2$, 130·54.

			°		°					°			°		
·00013	·00001	—	—	—	18	—	1114[1]	1185	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000261	·00002	—	—	—	18	—	1114	1185	—	—	—	—	—	—	
·000783	·00006	—	—	—	18	—	1100	1170	—	—	—	—	—	—	
·0013	·0001	—	—	—	18	—	1096	1165	—	—	·125	1084[4]	25	—	
·00261	·0002	—	—	—	18	—	1084	1152	—	—	·25	1070	25	—	[2] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·00783	·0006	—	—	—	18	—	1066	1133	—	—	·5	1047	25	—	
·013	·001	—	—	—	18	—	1054	1121	—	—	—	—	—	—	
·0261	·002	—	—	—	18	—	1033	1098	—	—	—	—	—	—	
·0783	·006	—	—	—	18	—	982	1044	—	—	·125	962[5]	20	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 381.
·1305	·01	—	—	—	18	·0224	951	1011	—	—	·25	938	20	—	
·391	·03	—	—	—	18	—	870	925	—	—	—	—	—	—	
·648	·05	1·0052	19·5	—	18	—	828	880	—	—	—	—	—	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 35.
·743	·057	1·0060	10·6	—	—	—	—	—	·602[3]	—	—	—	—	—	
1·29	·1	1·0113	19·5	—	18	—	755	802	—	—	—	—	—	—	
1·74	·135	1·0146	13·6	—	—	—	—	—	·620	—	—	—	—	—	
5·8	·466	1·0502	8·0	—	—	—	—	—	·641	—	—	—	—	—	[5] Mutzel, *Wied. Annal.* vol. xliii. p. 25.
6·20	·5	1·0520	19·5	—	18	·0241	531	564	—	—	—	—	—	—	
·00665	·00051	—	—	—	18	—	1010[2]	1073	—	—	—	—	—	—	
·0137	·00105	—	—	—	18	—	1000	1063	—	—	—	—	—	—	
·0249	·00191	—	—	—	18	—	980	1042	—	—	—	—	—	—	

Calcium Nitrate.

Equivalent Gramme Molecule, $\frac{1}{2}Ca(NO_3)_2$, 82·04.

3·98	·5	1·0307	18·0	314·0[1]	18	·0219	628	668	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
7·73	1·0	1·0608	18·0	541·0	18	·0219	541	575	—	—	—	—	—	—	
14·64	2·0	1·1202	18·0	818·0	18	·0217	409	435	—	—	—	—	—	—	
20·9	3·0	1·1781	18·0	946·0	18	·0217	315	335	—	—	·125	1092[2]	25	—	
26·57	4·0	1·2352	18·0	983·0	18	·0220	246	261	—	—	·25	1069	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
—	5·0	—	—	946·0	18	·0230	189	201	—	—	·5	1038	25	—	
—	6·0	—	—	845·0	18	·0250	141	150	—	—	1·0	978	25	—	
—	7·0	—	—	716·0	18	·0275	102	108	—	—	—	—	—	—	
—	8·0	—	—	584·0	18	·0302	73	78	—	—	—	—	—	—	
—	9·0	1·4984	18·0	461·0	18	·0331	51	54	—	—	—	—	—	—	
—	10·0	—	—	355·0	18	·0363	35	37	—	—	—	—	—	—	
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	

·0255	·00312	—	—	30·34[3]	18	—	971	1032	—	—	·125	961[5]	20	—	[3] Fitzpatrick, *Phil. Mag.* (5th series), vol. xxiv. p. 377.
·051	·00625	—	—	57·87	18	—	925	988	—	—	·25	927	20	—	
·102	·0125	—	—	112·2	18	—	898	955	—	—	·5	867	20	—	
·203	·025	—	—	209·6	18	—	838	891	—	—	1·0	766	20	—	
·407	·05	—	—	395·5	18	—	791	841	—	—	—	—	—	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 381.
·814	·1	1·0069	18·0	730·0	18	—	730	776	—	—	—	—	—	—	
·9	·11	1·0070	7·4	—	—	—	—	—	·613[4]	—	—	—	—	—	
1·62	·2	1·0135	18·0	1324·0	18	—	662	704	—	—	—	—	—	—	[5] Mutzel, *Wied. Annal.* vol. xliii. p. 26.
20·16	2·88	1·1707	7·4	—	—	—	—	—	·652	—	—	—	—	—	
41·32	7·15	1·3919	7·6	—	—	—	—	—	·718	—	—	—	—	—	

Magnesium Nitrate.

Equivalent Gramme Molecule, $\frac{1}{2}Mg(NO_3)_2$, 74·04.

3·612	·5	1·0249	21	309·0[1]	18	·0218	618	657	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
7·052	1·0	1·0499	21	546·0	18	·0215	546	580	—	—	—	—	—	—	
13·47	2·0	1·0994	21	890·0	18	·0211	445	473	—	—	·125	1072[3]	25	—	
19·34	3·0	1·1482	21	1096·0	18	·0207	365	388	—	—	·25	1051	25	—	
									—	—	·5	1010	25	—	[2] Fitzpatrick, *Phil. Mag.* (5th series), vol. xxiv. p. 377.
·0116	·00156	—	—	12·68[2]	18	—	811	862	—	—	1·0	934	25	—	
·0232	·00312	—	—	25·0	18	—	800	850	—	—	—	—	—	—	
·0465	·00625	—	—	48·7	18	—	779	828	—	—	·125	944[4]	20	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 37.
·093	·0125	—	—	93·4	18	—	747	794	—	—	·25	907	20	—	
·185	·025	—	—	182·4	18	—	730	776	—	—	·5	840	20	—	
·37	·05	—	—	343·5	18	—	687	730	—	—	1·0	720	20	—	
·737	·1	1·0051	21	643·6	18	—	644	685	—	—	—	—	—	—	[4] Mutzel, *Wied. Annal.* vol. xliii. p. 26.
1·465	·2	1·0099	21	1200·0	18	—	600	638	—	—	—	—	—	—	

Cadmium Nitrate.

Equivalent Gramme Molecule, $\frac{1}{2}Cd(NO_3)_2$, 117·9.

·0492	·00418	·9990	18	3·95[1]	18	·0234	935	994	—	—	—	—	—	—	[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 493.
·1	·00849	·9994	18	7·59	18	·0233	894	950	—	—	·125	1074[3]	25	—	
·249	·02123	1·0007	18	18·1	18	·0227	853	907	—	—	·25	1052	25	—	
·464	·03951	1·0025	18	32·5	18	·0230	823	875	—	—	·5	1017	25	—	
·952	·08146	1·0065	18	62·7	18	·0222	769	817	—	—	1·0	938	25	—	[2] Grotian, *Wied. Annal.* vol. xviii. p. 194.
1·014	·0868	1·0070	18	65·2[2]	18	·0226	751	798	—	—	—	—	—	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
5·02	·444	1·0416	18	270·0	18	·0221	608	646	—	—	—	—	—	—	
10·07	·930	1·0875	18	480·0	18	·0215	516	548	—	—	—	—	—	—	

Cadmium Nitrate—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}Cd(NO_3)_2$, 117·9.

			°		°				°				°		
20·2	2·047	1·1926	18	773·0	18	·0212	377	401	—	—	—	—	—	—	
30·0	3·345	1·3124	18	891·0	18	·0214	266	283	—	—	—	—	—	—	
40·0	4·957	1·4589	18	841·0	18	·0228	169	179	—	—	—	—	—	—	
48·3	6·580	1·6034	18	697·0	18	·0253	106	113	—	—	—	—	—	—	

Lead Nitrate.

Equivalent Gramme Molecule, $\frac{1}{2}Pb(NO_3)_2$, 165·1.

·0081	·00049	—	—	—	—	·0231	1100[1]	1169	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·0125	·00076	—	—	—	—	—	1060	1127	—	—	—	—	—	—	
·0248	·0015	—	—	—	—	—	1010	1074	—	—	—	—	—	—	
5·0	·317	1·0449	15	179[2]	18	·0238	565	601	—	—	·125	1086[3]	25	—	[2] Long, *Wied. Annal.* vol. xi. p. 37.
10·0	·663	1·0937	15	301	18	·0251	454	483	—	—	·25	1074	25	—	
15·0	1·042	1·1467	15	401	18	·0251	385	409	—	—	·5	1049	25	—	
20·0	1·460	1·2043	15	487	18	·0250	334	355	—	—	1·0	993	25	—	[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
25·0	1·920	1·2678	15	561	18	·0252	292	310	—	—	—	—	—	—	
30·0	2·427	1·3358	15	625	18	·0257	216	230	—	—	—	—	—	—	

Chloric Acid.

Equivalent Gramme Molecule, $HClO_3$, 84·25.

·0082	·000976	—	—	384·8[1]	25	—	—	4090[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 75.
·0165	·00195	—	—	381·5	25	—	—	4055	—	—	—	—	—	—	
·033	·0039	—	—	377·0	25	—	—	4087	—	—	—	—	—	—	
·066	·0078	—	—	371·0	25	—	—	3944	—	—	—	—	—	—	[2] At 25°.
·132	·0156	—	—	363·8	25	—	—	3867	—	—	—	—	—	—	
·262	·0312	—	—	355·4	25	—	—	3778	—	—	—	—	—	—	

Potassium Chlorate.

Equivalent Gramme Molecule, $KClO_3$, 122·59.

·000122	·00001	—	—	—	18	—	1141[1]	1213	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000245	·00002	—	—	—	18	—	1135	1206	—	—	—	—	—	—	
·000735	·00006	—	—	—	18	—	1126	1197	—	—	—	—	—	—	
·00122	·0001	—	—	—	18	—	1122	1193	—	—	—	—	—	—	
·00245	·0002	—	—	—	18	—	1119	1190	—	—	—	—	—	—	

·00735	·0006	—	—	—	18	—	1109	1179	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 375.
·01226	·001	—	—	—	18	—	1101	1171	—	—	—	—	—	—	
·0245	·002	—	—	—	18	—	1091	1160	—	—	—	—	—	—	
·0735	·006	—	—	—	18	—	1068	1135	—	—	—	—	—	—	[3] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·1226	·01	—	—	—	18	·0219	1053	1120	—	—	—	—	—	—	
·367	·03	—	—	—	18	—	1006	1069	—	—	—	—	—	—	
·609	·05	—	—	—	18	—	976	1037	—	—	—	—	—	—	
·86	—	—	—	—	—	—	—	—	·462[2]	—	—	—	—	—	
1·215	·1	1·0085	19·5	—	18	—	927	985	—	—	—	—	—	—	
3·62	—	—	—	—	—	—	—	—	·445	—	—	—	—	—	
5·903	·5	1·0384	19·5	—	18	·0212	799	849	—	—	—	—	—	—	
·012	·000976	—	—	130·2[3]	25	—	—	1200	—	—	—	—	—	—	
·024	·00195	—	—	126·8	25	—	—	1169	—	—	—	—	—	—	
·048	·0039	—	—	123·3	25	—	—	1136	—	—	—	—	—	—	
·096	·0078	—	—	120·0	25	—	—	1106	—	—	—	—	—	—	
·191	·0156	—	—	116·6	25	—	—	1075	—	—	—	—	—	—	
·382	·0312	—	—	112·5	25	—	—	1037	—	—	—	—	—	—	

Sodium Chlorate.

Equivalent Gramme Molecule, $NaClO_3$, 106·5.

—	—	—	—	—	—	—	—	—	—	—	1·168[3]	891	20	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 81.
·0104	·000976	—	—	106·6[1]	25	—	—	1133[2]	—	—	2·23	785	20	—	
·0208	·00195	—	—	104·1	25	—	—	1106	—	—	3·992	586	20	—	[2] At 25°.
·0415	·0039	—	—	101·5	25	—	—	1079	—	—	—	—	—	—	
·0825	·0078	—	—	98·6	25	—	—	1048	—	—	—	—	—	—	[3] Sprung, *Pogg. Annal.* vol. cvi. p. 15.
·165	·0156	—	—	95·8	25	—	—	1018	—	—	—	—	—	—	
·331	·0312	—	—	92·7	25	—	—	985	—	—	—	—	—	—	

Lithium Chlorate.

Equivalent Gramme Molecule, $LiClO_3$, 90·48.

·00877	·000976	—	—	97·0[1]	25	—	—	1031[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 83.
·01755	·00195	—	—	94·2	25	—	—	1001	—	—	—	—	—	—	
·0351	·0039	—	—	91·9	25	—	—	977	—	—	—	—	—	—	
·0702	·0078	—	—	89·1	25	—	—	947	—	—	—	—	—	—	
·1405	·0156	—	—	86·4	25	—	—	918	—	—	—	—	—	—	[2] At 25°.
·281	·0312	—	—	83·7	25	—	—	890	—	—	—	—	—	—	

Perchloric Acid.

Equivalent Gramme Molecule, $HClO_4$, 100·46.

			°		°				°				°		
·00976	·000976	—	—	395·5[1]	25	—	—	4204[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 76.
·00195	·00195	—	—	391·0	25	—	—	4156	—	—	—	—	—	—	
·039	·0039	—	—	384·8	25	—	—	4090	—	—	—	—	—	—	
·078	·0078	—	—	378·0	25	—	—	4018	—	—	—	—	—	—	
·156	·0156	—	—	369·5	25	—	—	3928	—	—	—	—	—	—	[2] At 25°.
·313	·0312	—	—	361·2	25	—	—	3840	—	—	—	—	—	—	

Potassium Perchlorate.

Equivalent Gramme Molecule, $KClO_4$, 138·59.

·0135	·000976	—	—	139·81[1]	25	—	—	1486[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·027	·00195	—	—	136·4	25	—	—	1450	—	—	—	—	—	—	
·054	·0039	—	—	132·8	25	—	—	1412	—	—	—	—	—	—	
·108	·0078	—	—	129·2	25	—	—	1373	—	—	—	—	—	—	[2] At 25°.
·216	·0156	—	—	124·8	25	—	—	1327	—	—	—	—	—	—	
·431	·0312	—	—	120·7	25	—	—	1283	—	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 373.
·833	—	—	—	—	—	—	—	—	·463[3]	—	—	—	—	—	

Sodium Perchlorate.

Equivalent Gramme Molecule, $NaClO_4$, 122·5.

·0119	·000976	—	—	116·1[1]	25	—	—	1234[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·0238	·00195	—	—	113·3	25	—	—	1204	—	—	—	—	—	—	
·0475	·0039	—	—	110·8	25	—	—	1178	—	—	—	—	—	—	
·095	·0078	—	—	108·2	25	—	—	1150	—	—	—	—	—	—	
·19	·0156	—	—	105·2	25	—	—	1118	—	—	—	—	—	—	[2] At 25°.
·38	·0312	—	—	102·0	25	—	—	1084	—	—	—	—	—	—	

Lithium Perchlorate.

Equivalent Gramme Molecule, $LiClO_4$, 106·48.

·0104	·000976	—	—	107·4[1]	25	—	—	1142	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 85.
·0208	·00195	—	—	104·4	25	—	—	1119[2]	—	—	—	—	—	—	
·0415	·0039	—	—	101·6	25	—	—	1080	—	—	—	—	—	—	
·083	·0078	—	—	98·9	25	—	—	1051	—	—	—	—	—	—	
·166	·0156	—	—	95·9	25	—	—	1019	—	—	—	—	—	—	[2] At 25°.
·331	·0312	—	—	92·9	25	—	—	987	—	—	—	—	—	—	

Sulphuric Acid.

Equivalent Gramme Molecule, $\frac{1}{2}H_2SO_4$, 49·035.

·000049	·00001	—	—	—	18	—	1413[1]	1502	—	—	—	—	—	—
·000098	·00002	—	—	—	18	—	2077	2208	—	—	—	—	—	—
·000294	·00006	—	—	—	18	—	2927	3111	—	—	—	—	—	—
·00049	·0001	—	—	—	18	—	3118	3314	—	—	—	—	—	—
·00098	·0002	—	—	—	18	—	3280	3486	—	—	·125[4]	927	18	—
·00294	·0006	—	—	—	18	—	3342	3552	—	—	·25	914	18	—
·0049	·001	—	—	—	18	—	3316	3524	—	—	·5	895	18	—
·0098	·002	—	—	—	18	·0159	3240	3444	—	—	1·0	857	18	—
·0294	·006	—	—	—	18	—	3001	3190	—	—	—	—	—	—
·049	·01	—	—	—	18	·0125	2855	3035	—	—	—	—	—	—
·147	·03	—	—	—	18	—	2515	2673	—	—	—	—	—	—
·245	·05	—	—	—	18	—	2343	2490	—	—	2·176[5]	756	18	·0249
·489	·1	1·0027	15	—	18	—	2084	2215	—	—	4·522	603	18	·0237
·616	—	—	—	—	—	—	—	—	·206[3]	—	7·438	457	18	·0258
1·01	—	—	—	—	—	—	—	—	·212	—	10·61	344	18	·0249
2·414	·5	1·0155	15	—	18	—	1899	2018	—	—	14·33	242	18	·0242
4·1	—	—	—	—	—	—	—	—	·177	—	18·25	160	18	·0259
4·758	1·0	1·0304	15	—	18	—	1820	1935	—	—	23·17	86	18	·0302
13·44	3·0	1·0941	15	—	18	—	1560	1658	—	—	29·28	37	18	·0423
15·59	—	—	—	—	—	—	—	—	·174	—	30·8	34	18	·0432
21·25	5·0	1·1534	15	—	18	—	1270	1350	—	—	32·18	34	18	·0421
38·03	10·0	1·2894	15	—	18	—	660	701	—	—	—	—	—	—
41·0	—	—	—	—	—	—	—	—	·288	—	—	—	—	—
64·22	—	—	—	—	—	—	—	—	·4	—	—	—	—	—
·098	·02	—	—	51·9[2]	18	—	2595	2758	—	—	—	—	—	—
·196	·04	—	—	95·3	18	—	2382	2532	—	—	—	—	—	—
·391	·08	1·0020	15	175·6	18	—	2195	2333	—	—	—	—	—	—
·78	·16	1·0048	15	326·9	18	—	2043	2171	—	—	—	—	—	—
1·553	·32	1·0100	15	613·8	18	—	1918	2038	—	—	—	—	—	—

[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.

[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.

[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 401.

[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.

[5] Grotian, *Wied. Annal.* vol. viii. p. 543.

Potassium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}K_2SO_4$, 87·16.

·000087	·00001	—	—	—	18	—	1275[1]	1355	—	—	—	—	—	—
·000174	·00002	—	—	—	18	—	1266	1346	—	—	—	—	—	—
·000523	·00006	—	—	—	18	—	1254	1333	—	—	—	—	—	—

[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.

Potassium Sulphate—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}K_2SO_4$, 87·16.

			°		°					°					
·00087	·0001	—	—	—	18	—	1249	1328	—	—	·618	916[5]	20	·0244	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·00174	·0002	—	—	—	18	—	1241	1319	—	—	1·209	861	20	·0235	
·00523	·0006	—	—	—	18	—	1220	1297	—	—	—	—	—	—	
·0087	·001	—	—	—	18	—	1207	1283	—	—	—	—	—	—	
·0174	·002	—	—	—	18	—	1181	1256	—	—	1·0	888[6]	20	—	[3] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0523	·006	—	—	—	18	—	1430	1201	—	—	—	—	—	—	
·0871	·01	—	—	—	18	·0223	1098	1167	—	—	·125	966[7]	20	—	
·241	·028	1·0020	6·6	—	—	—	—	—	·498[4]	—	·25	954	20	—	[4] Hittorf, *Pogg. Annal.* vol. xcviii. p. 27.
·261	·03	1·0015	15·0	—	18	—	1008	1071	—	—	·5	928	20	—	
·434	·05	1·0030	15·0	—	18	—	959	1019	—	—	1·0	883	20	—	
·866	·1	1·0069	15·0	—	18	—	897	954	—	—	—	—	—	—	
4·212	·5	1·0345	15·0	—	18	·0218	736	782	—	—	—	—	—	—	
7·67	·936	1·0639	12·0	—	—	—	—	—	·499	—	—	—	—	—	[5] Sprung, *Pogg. Annal.* vol. clix. p. 16.
8·163	1·0	1·0677	15·0	—	18	·0209	672	714	—	—	—	—	—	—	
·542	·0625	1·0040	15·0	57·0[2]	18	—	912	969	—	—	—	—	—	—	[6] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·629	·0725	1·0047	15·0	65·5	18	—	903	960	—	—	—	—	—	—	
1·080	·125	1·0088	15·0	106·0	18	—	848	899	—	—	—	—	—	—	
1·251	·145	1·0102	15·0	121·0	18	—	834	889	—	—	—	—	—	—	
2·477	·29	1·0202	15·0	223·0	18	—	769	817	—	—	—	—	—	—	
4·212	·5	1·0345	15·0	361·0	18	—	722	767	—	—	—	—	—	—	[7] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 37.
·00558	·00064	—	—	—	18	·c238	1250[3]	1329	—	—	—	—	—	—	
·0074	·00085	—	—	—	18	·0237	1210	1286	—	—	—	—	—	—	
·0135	·00155	—	—	—	18	·0239	1160	1233	—	—	—	—	—	—	
·0286	·00325	—	—	—	18	·0231	1090	1159	—	—	—	—	—	—	
·0862	·0099	—	—	—	18	·0223	1020	1084	—	—	—	—	—	—	

Ammonium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}(NH_4)_2SO_4$, 66·075.

3·236	·5	1·0186	15	351[1]	18	·0221	702	746	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 150.
6·360	1·0	1·0366	15	643	18	·0212	643	683	—	—	—	—	—	—	
12·312	2·0	1·0708	15	1130	18	·0201	565	601	—	—	1·282	853[3]	20	·0238	
17·926	3·0	1·1032	15	1535	18	·0195	512	544	—	—	2·637	745	20	·0229	
—	4·0	—	—	1856	18	·0193	464	493	—	—	4·438	600	20	·0231	

28·336	5·0	1·1632	15	2087	18	·0192	417	443	—	—	—	—	—	—	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	6·0	—	—	2233	18	·0193	372	395	—	—	—	—	—	—	
·411	·0625	1·0018	15	56[2]	18	—	896	952	—	—	—	—	—	—	[3] Sprung, *Pogg. Annal.* vol. clix. p. 16.
·820	·125	1·0045	15	103	18	—	824	876	—	—	—	—	—	—	
1·632	·25	1·0095	15	190	18	—	760	808	—	—	—	—	—	—	
3·236	·5	1·0186	15	347	18	—	694	738	—	—	—	—	—	—	

Sodium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}Na_2SO_4$, 71·075.

·000071	·00001	—	—	—	18	—	1054[1]	1121	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000142	·00002	—	—	—	18	—	1056	1123	—	—	—	—	—	—	
·000426	·00006	—	—	—	18	—	1038	1103	—	—	—	—	—	—	
·00071	·0001	—	—	—	18	—	1034	1099	—	—	·485	880[5]	20	·0255	
·00142	·0002	—	—	—	18	—	1026	1091	—	—	·989	795	20	·0247	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·00426	·0006	—	—	—	18	—	1009	1072	—	—	1·996	630	20	·0257	
·0071	·001	—	—	—	18	—	998	1060	—	—	—	—	—	—	
·0142	·002	—	—	—	18	—	980	1042	—	—	1·0	796[6]	20	—	
·0426	·006	—	—	—	18	—	933	992	—	—	—	—	—	—	[3] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·071	·01	—	—	—	18	·0240	906	963	—	—	·125	948[7]	20	—	
·213	·03	—	—	—	18	·0240	828	880	—	—	·25	922	20	—	
·355	·05	—	—	—	18	—	784	833	—	—	·5	877	20	—	
·706	·1	1·0062	15	—	18	—	734	780	—	—	1·0	789	20	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 377.
1·93	·276	1·0181	9	—	—	—	—	—	·634[4]	—	—	—	—	—	
3·542	·5	1·0317	15	—	18	·0232	559	594	—	—	—	—	—	—	[5] Sprung, *Pogg. Annal.* vol. clix. p. 15.
6·70	1·0	1·0612	15	—	18	·0242	475	505	—	—	—	—	—	—	
7·83	1·18	1·0735	9	—	—	—	—	—	·641	—	—	—	—	—	
12·70	2·0	1·1190	15	—	18	·0254	376	400	—	—	—	—	—	—	
·444	·0625	—	—	46·7[2]	18	—	747	794	—	—	—	—	—	—	[6] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·881	·125	1·0080	15	85·5	18	—	684	727	—	—	—	—	—	—	
1·750	·25	1·0158	15	154·0	18	—	616	654	—	—	—	—	—	—	
3·542	·5	1·0317	15	272·0	18	—	544	578	—	—	—	—	—	—	
·00604	·00085	—	—	—	18	—	1010[8]	1074	—	—	—	—	—	—	[7] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 39.
·00974	·00137	—	—	—	18	—	970	1031	—	—	—	—	—	—	
·01834	·00258	—	—	—	18	—	940	999	—	—	—	—	—	—	

Lithium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}Li_2SO_4$, 55·05.

			°		°					°			°		
·000055	·00001	—	—	—	18	—	949[1]	1008	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·00011	·00002	—	—	—	18	—	950	1009	—	—	—	—	—	—	
·00033	·00006	—	—	—	18	—	950	1009	—	—	—	—	—	—	
·00055	·0001	—	—	—	18	—	945	1004	—	—	—	—	—	—	
·0011	·0002	—	—	—	18	—	937	996	—	—	1·0	712[3]	17·6	—	[2] Kuschel, *Wied. Annal.* vol. xiii. p. 300.
·0033	·0006	—	—	—	18	—	918	976	—	—	—	—	—	—	
·0055	·001	—	—	—	18	—	906	963	—	—	—	—	—	—	
·011	·002	—	—	—	18	—	885	941	—	—	·125	1059[4]	25·0	—	[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·033	·006	—	—	—	18	—	844	897	—	—	·25	1026	25·0	—	
·055	·01	—	—	—	18	·0242	818	870	—	—	·5	961	25·0	—	
·165	·03	—	—	—	18	—	742	789	—	—	1·0	847	25·0	—	
·275	·05	—	—	—	18	—	701	745	—	—	—	—	—	—	
—	·09	—	—	—	—	—	—	—	·595[2]	—	—	—	—	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 38.
·548	·1	—	—	—	18	—	637	677	—	—	—	—	—	—	
—	·159	—	—	—	—	—	—	—	·649	—	—	—	—	—	
2·7	·5	—	—	—	18	·0236	474	504	—	—	—	—	—	—	
5·27	1·0	1·0445	18·6	—	18	·0237	386	410	—	—	—	—	—	—	
—	2·0	—	—	—	18	·0240	287	305	—	—	—	—	—	—	

Silver Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}Ag_2SO_4$, 155·9.

·0071	·00046	—	—	—	18	—	1090[1]	1159	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·0124	·00080	—	—	—	18	—	1050	1116	—	—	—	—	—	—	
·0263	·00169	—	—	—	18	—	1010	1073	—	—	—	—	—	—	
·0473	·00344	—	—	—	18	—	970	1031	—	—	—	—	—	—	

Magnesium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}MgSO_4$, 60·035.

·00006	·00001	—	—	—	18	—	1056[1]	1123	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·00012	·00002	—	—	—	18	—	1052	1119	—	—	—	—	—	—	
·00036	·00006	—	—	—	18	—	1036	1101	—	—	—	—	—	—	
·0006	·0001	—	—	—	18	—	1034	1099	—	—	—	—	—	—	
·0012	·0002	—	—	—	18	—	1015	1079	—	—	·8715	746[2]	20	·0258	[2] Sprung, *Pogg. Annal.* vol. clix. p. 19.
·0036	·0006	—	—	—	18	—	967	1028	—	—	1·738	554	20	·0283	

·006	·001	—	—	—	18	—	935	994	—	—	2·69	393	20	·0306
·012	·002	—	—	—	18	—	881	937	—	—	3·9	249	20	·0332
·036	·006	—	—	—	18	—	773	822	—	—	—	—	—	—
·06	·01	—	—	—	18	·0236	715	760	—	—	1·0	711[5]	20	—
·18	·03	—	—	—	18	—	587	624	—	—	—	—	—	—
·299	·05	1·0025	15·0	—	18	—	532	565	—	—	·125	937[6]	20	—
·475	·0795	1·0048	4·8	—	—	—	—	—	·656[4]	—	·25	896	20	—
·597	·1	1·0058	15·0	—	18	—	474	504	—	—	·5	831	20	—
2·912	·5	1·0300	15·0	—	18	·0222	330	351	—	—	1·0	701	20	—
5·67	1·0	1·0587	15·0	—	18	·0229	270	287	—	—	—	—	—	—
15·43	3·0	1·1673	15·0	—	18	·0254	151	160	—	—	—	—	—	—
15·92	3·12	1·1763	3·6	—	—	—	—	—	·762	—	—	—	—	—
·00575	·000976	—	—	1133[3]	25	—	—	1023	—	—	—	—	—	—
·0117	·00195	—	—	1055	25	—	—	952	—	—	—	—	—	—
·0234	·0039	—	—	966	25	—	—	876	—	—	—	—	—	—
·0468	·0078	—	—	869	25	—	—	790	—	—	—	—	—	—
·0935	·0156	—	—	772	25	—	—	703	—	—	—	—	—	—
·187	·0312	—	—	678	25	—	—	618	—	—	—	—	—	—

[3] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 109.

[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 382.

[5] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.

[6] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 38.

Zinc Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}ZnSO_4$, 80·58.

·00008	·00001	—	—	—	18	—	1060[1]	1127	—	—	—	—	—	—
·000161	·00002	—	—	—	18	—	1047	1113	—	—	—	—	—	—
·000483	·00006	—	—	—	18	—	1032	1097	—	—	—	—	—	—
·0008	·0001	—	—	—	18	—	1023	1088	—	—	·0625	946[3]	20	—
·00161	·0002	—	—	—	18	—	1001	1064	—	—	·125	925	20	—
·00483	·0006	—	—	—	18	—	953	1013	—	—	·25	886	20	—
·008	·001	—	—	—	18	—	919	977	—	—	·5	817	20	—
·0161	·002	—	—	—	18	—	861	915	—	—	1·0	701	20	—
·0483	·006	—	—	—	18	—	744	791	—	—	—	—	—	—
·08	·01	—	—	—	18	·0234	685	728	—	—	1·0	723[4]	20	—
·242	·03	—	—	—	18	—	556	591	—	—	—	—	—	—
·373	—	—	—	—	—	—	—	—	·636[2]	—	·986	708[5]	20	·028
·4	·05	1·0041	15	—	18	—	500	530	—	—	1·537	595	20	·0297
·799	·1	1·0090	15	—	18	—	431	458	—	—	2·144	478	20	·0313
3·85	·5	1·0404	15	—	18	·0226	302	321	—	—	2·993	349	20	·0341

[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.

[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 385.

[3] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 40.

[4] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.

[5] Grotian, *Pogg. Annal.* vol. clx. p. 263.

ZINC SULPHATE—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}ZnSO_4$, 80·58.

			°		°					°			°		
7·456	1·0	1·0807	15	—	18	·0224	249	265	—	—	3·555	284	20	·0338	[6] Bouty, *Journ. de Physique*, vol. vi. p. 13.
19·637	3·0	1·2310	15	—	18	·0241	146	155	—	—	5·085	161	20	·0384	
19·8	—	—	—	—	—	—	—	—	·760	—	—	—	—	—	
28·38	—	—	—	—	—	—	—	—	·778	—	—	—	—	—	
29·36	5·0	1·372	15	—	18	·0277	82	87	—	—	—	—	—	—	[7] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
·008	·001	—	—	1·02[6]	18	—	—	980	—	—	—	—	—	—	
·080	·01	—	—	7·38	18	—	—	734	—	—	—	—	—	—	[8] Beetz, *Pogg. Annal.* vol. cxvii. p. 9.
·799	·1	1·0090	15	46·46	18	—	—	466	—	—	—	—	—	—	
1·583	·2	1·0179	15	77·3	18	—	—	386	—	—	—	—	—	—	
3·85	·5	1·0404	15	152·0	18	—	—	304	—	—	—	—	—	—	
·00459	·00057	—	—	—	18	—	950[7]	1010	—	—	—	—	—	—	
·00604	·00075	—	—	—	18	—	910	967	—	—	—	—	—	—	
·0104	·00129	—	—	—	18	—	850	903	—	—	—	—	—	—	
·0270	·00335	—	—	—	18	—	760	808	—	—	—	—	—	—	
7·18	·961	1·0780	15	228·0[8]	18	—	—	252	—	—	—	—	—	—	
9·34	1·276	1·1012	15	274·0	18	—	—	228	—	—	—	—	—	—	
11·88	1·668	1·1317	15	319·0	18	—	—	203	—	—	—	—	—	—	
15·60	2·282	1·1790	15	378·0	18	—	—	176	—	—	—	—	—	—	
17·75	2·656	1·2063	15	425·0	18	—	—	170	—	—	—	—	—	—	
19·61	2·996	1·2310	15	430·0	18	—	—	153	—	—	—	—	—	—	
20·41	3·148	1·2430	15	431·0	18	—	—	146	—	—	—	—	—	—	
22·44	3·539	1·2710	15	440·0	18	—	—	132	—	—	—	—	—	—	
22·59	3·574	1·2746	15	440·0	18	—	—	131	—	—	—	—	—	—	
23·15	3·603	1·2832	15	441·0	18	—	—	130	—	—	—	—	—	—	
23·66	3·788	1·2901	15	445·0	18	—	—	125	—	—	—	—	—	—	
24·88	3·913	1·2986	15	442·0	18	—	—	120	—	—	—	—	—	—	
25·28	4·116	1·3120	15	439·0	18	—	—	113	—	—	—	—	—	—	
26·81	4·448	1·3370	15	431·0	18	—	—	103	—	—	—	—	—	—	
32·50	5·752	1·4260	15	374·0	18	—	—	69	—	—	—	—	—	—	
33·71	—	—	—	359·0	18	—	—	—	—	—	—	—	—	—	
35·04	—	—	—	336·0	18	—	—	—	—	—	—	—	—	—	
37·81	—	—	—	294·0	18	—	—	—	—	—	—	—	—	—	

COPPER SULPHATE.

Equivalent Gramme Molecule, $\frac{1}{2}CuSO_4$, 79·78.

·00008	·00001	—	—	—	18	—	1086[1]	1154	—	—	—	—	—	—
·00016	·00002	—	—	—	18	—	1084	1152	—	—	—	—	—	—
·00048	·00006	—	—	—	18	—	1074	1142	—	—	—	—	—	—
·0008	·0001	—	—	—	18	—	1062	1129	—	—	—	—	—	—
·0048	·0006	—	—	—	18	—	987	1049	—	—	1·0	675[4]	17·6	—
·008	·001	—	—	—	18	—	950	1009	—	—	·0625	1073[5]	25·0	—
·016	·002	—	—	—	18	—	873	928	—	—	·125	1052	25·0	—
·048	·006	—	—	—	18	—	740	787	—	—	·25	1012	25·0	—
·08	·01	—	—	—	18	·0229	675	717	—	—	·5	942	25·0	—
·239	·03	1·0015	18·0	—	18	—	537	571	—	—	1·0	805	25·0	—
·397	·05	1·0034	18·0	—	18	—	479	509	—	—	—	—	—	—
·671	·0846	1·0071	4·4	—	—	—	—	—	·638[3]	4·4	—	—	—	—
·791	·1	1·0078	18·0	—	18	—	424	451	—	—	—	—	—	—
1·282	·163	1·0135	4·8	—	—	—	—	—	·651	4·3	—	—	—	—
2·457	·315	1·0254	3·0	—	—	—	—	—	·644	4·5	—	—	—	—
3·847	·5	1·0386	18·0	—	18	·0216	288	306	—	—	—	—	—	—
5·235	·692	1·0553	3·6	—	—	—	—	—	·675	5·5	—	—	—	—
7·418	1·0	1·0758	18·0	—	18	·0218	241	256	—	—	—	—	—	—
9·47	1·31	1·1036	4·9	—	—	—	—	—	·712	6·5	—	—	—	—
13·6	1·962	1·1521	4·5	—	—	—	—	—	·724	5·5	—	—	—	—
—	3·0	—	—	—	18	·0241	150	159	—	—	—	—	—	—
·00486	·00061	—	—	—	18	—	1020[2]	1084	—	—	—	—	—	—
·00622	·00078	—	—	—	18	—	970	1031	—	—	—	—	—	—
·00989	·00124	—	—	—	18	—	950	1010	—	—	—	—	—	—
·0156	·00196	—	—	—	18	—	840	893	—	—	—	—	—	—
·0251	·00315	—	—	—	18	—	800	850	—	—	—	—	—	—
·0411	·0064	—	—	—	18	—	700	744	—	—	—	—	—	—

[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.

[2] Vicentini, *Atti. Acad. Torino*, vol. xx. p. 689.

[3] Hittorf, *Pogg. Annal.* vol. xcviii. p. 196.

[4] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.

[5] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 38.

CADMIUM SULPHATE.

Equivalent Gramme Molecule, $\frac{1}{2}CdSO_4$, 104·03.

·0289	·00278	·99893	18	2·3[1]	18	·0230	827	879	—	—	—	—	—	—
·0489	·00482	·99915	18	3·62	18	·0230	750	797	—	—	—	—	—	—

[1] Wershoven, *Zeitschrift für physik. Chemie*, vol. v. p. 494.

Cadmium Sulphate—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}CdSO_4$, 104·03.

			°		°					°			°		
·0999	·00961	·99961	18	6·43	18	·0222	668	710	—	—	·125	1057[4]	25	—	[2] Grotian, *Wied. Annal.* vol. xviii. p. 193.
—	—	—	—	—	—	—	—	—	—	—	·25	1014	25	—	
·495	·0479	1·0034	18	22·24	18	·0211	459	499	—	—	·5	944	25	—	
·981	·0954	1·0084	18	37·82	18	·0207	396	421	—	—	1·0	811	25	—	
·282	·0272	1·0015	18	14·3[2]	18	·0221	525	558	—	—	—	—	—	—	[3] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 689.
1·011	·0983	1·0085	18	38·9	18	·0210	396	421	—	—	—	—	—	—	
5·08	·514	1·0495	18	137·0	18	·0206	266	283	—	—	—	—	—	—	
10·11	1·076	1·1039	18	232·0	18	·0206	216	230	—	—	—	—	—	—	[4] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 36.
25·03	3·127	1·2955	18	400·0	18	·0223	128	136	—	—	—	—	—	—	
36·07	5·133	1·4756	18	392·0	18	·0255	76	81	—	—	—	—	—	—	
·00655	·00063	—	—	—	18	—	930[3]	989	—	—	—	—	—	—	
·00936	·0009	—	—	—	18	—	890	946	—	—	—	—	—	—	
·01633	·00157	—	—	—	18	—	820	871	—	—	—	—	—	—	

Ferrous Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}FeSO_4$, 76·03.

·00684	·0009	—	—	—	18	·0296	780[1]	829	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·00973	·00128	—	—	—	18	·0230	760	808	—	—	—	—	—	—	
·01193	·00157	—	—	—	18	·0270	730	776	—	—	—	—	—	—	
·02417	·00318	—	—	—	18	—	670	712	—	—	—	—	—	—	

Nickel Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}NiSO_4$, 77·33.

—	—	—	—	—	—	—	—	—	—	—	·125	1059[2]	25	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·00572	·00074	—	—	—	18	—	730[1]	776	—	—	·25	1016	25	—	
·00727	·00094	—	—	—	18	—	720	765	—	—	·5	941	25	—	
·01392	·0018	—	—	—	18	—	680	723	—	—	1·0	803	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 39.

Cobalt Sulphate.

Equivalent Gramme Molecule, $\frac{1}{2}CoSO_4$, 77·53.

—	—	—	—	—	—	—	—	—	—	—	·125	1050[2]	25	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·00729	·00094	—	—	—	18	—	810[1]	861	—	—	·25	1015	25	—	
·01046	·00135	—	—	—	18	—	780	829	—	—	·5	942	25	—	
·02054	·00265	—	—	—	18	—	700	744	—	—	1·0	807	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 39.

Aluminium Sulphate.

Equivalent Gramme Molecule, $\frac{1}{6}Al_2(SO_4)_3$, 41·02.

·00266	·00065	—	—	—	18	—	810[1]	861	—	—	·125	1053[2]	25	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 690.
·00640	·00156	—	—	—	18	—	700	744	—	—	·25	1010	25	—	
·00865	·00211	—	—	—	18	—	660	701	—	—	·5	927	25	—	
—	—	—	—	—	—	—	—	—	—	—	1·0	777	25	—	[2] Wagner, *Zeitschrift für physik. Chemie*, vol. v. p. 39.

Methyl Sulphuric Acid.

Equivalent Gramme Molecule, HCH_3SO_4, 112·07.

·0109	·000976	—	—	368·1[1]	25	—	—	3913[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 76.
·0218	·00195	—	—	365·2	25	—	—	3882	—	—	—	—	—	—	
·0435	·0039	—	—	362·8	25	—	—	3857	—	—	—	—	—	—	
·087	·0078	—	—	357·8	25	—	—	3803	—	—	—	—	—	—	[2] At 25°.
·174	·0156	—	—	351·4	25	—	—	3735	—	—	—	—	—	—	
·349	·0312	—	—	345·0	25	—	—	3667	—	—	—	—	—	—	

Sodium Methyl Sulphate.

Equivalent Gramme Molecule, $NaCH_3SO_4$, 134·1.

·0130	·000976	—	—	91·4[1]	25	—	—	972[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 81.
·0261	·00195	—	—	89·2	25	—	—	948	—	—	—	—	—	—	
·0522	·0039	—	—	86·9	25	—	—	924	—	—	—	—	—	—	
·1045	·0078	—	—	84·8	25	—	—	901	—	—	—	—	—	—	[2] At 25°.
·209	·0156	—	—	82·2	25	—	—	874	—	—	—	—	—	—	
·418	·0312	—	—	79·6	25	—	—	846	—	—	—	—	—	—	

Ethyl Sulphuric Acid.

Equivalent Gramme Molecule, $HC_2H_5SO_4$, 126·07.

			°		°				°				°		
·0122	·000976	—	—	367·4[1]	25	—	—	390·5[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 76.
·0245	·00195	—	—	363·9	25	—	—	3868	—	—	—	—	—	—	
·049	·0039	—	—	359·3	25	—	—	3819	—	—	—	—	—	—	
·098	·0078	—	—	353·4	25	—	—	3757	—	—	—	—	—	—	
·196	·0156	—	—	347·6	25	—	—	3695	—	—	—	—	—	—	[2] At 25°.
·392	·0312	—	—	340·9	25	—	—	3624	—	—	—	—	—	—	

Sodium Ethyl Sulphate.

Equivalent Gramme Molecule, $NaC_2H_5SO_4$, 148·1.

·0144	·000976	—	—	87·5[1]	25	—	—	930[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 81.
·0289	·00195	—	—	85·3	25	—	—	907	—	—	—	—	—	—	
·0578	·0039	—	—	83·4	25	—	—	886	—	—	—	—	—	—	
·1155	·0078	—	—	82·1	25	—	—	873	—	—	—	—	—	—	
·231	·0156	—	—	79·8	25	—	—	848	—	—	—	—	—	—	[2] At 25°.
·462	·0312	—	—	77·2	25	—	—	821	—	—	—	—	—	—	

Sulphurous Acid.

Equivalent Gramme Molecule, $\frac{1}{2}H_2SO_3$, 41·03.

·002	·000498	—	—	83·6[1]	25	—	—	1888[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 314.
·004	·000976	—	—	80·4	25	—	—	1815	—	—	—	—	—	—	
·008	·00195	—	—	77·1	25	—	—	1741	—	—	—	—	—	—	
·016	·0039	—	—	72·5	25	—	—	1637	—	—	—	—	—	—	
·032	·0078	—	—	66·5	25	—	—	1501	—	—	—	—	—	—	[2] At 25°.
·064	·0156	—	—	58·9	25	—	—	1330	—	—	—	—	—	—	
·128	·0312	—	—	50·1	25	—	—	1132	—	—	—	—	—	—	
·256	·0625	—	—	41·6	25	—	—	939	—	—	—	—	—	—	
·512	·125	—	—	32·8	25	—	—	741	—	—	—	—	—	—	
—	·25	—	—	25·4	25	—	—	574	—	—	—	—	—	—	
—	·5	—	—	19·2	25	—	—	434	—	—	—	—	—	—	

Selenic Acid.

Equivalent Gramme Molecule, $\frac{1}{2}H_2SeO_4$, 72·4.

·00176	·000244	—	—	173·4[1]	25	—	—	3915[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 313.
·00352	·000488	—	—	174·4	25	—	—	3937	—	—	—	—	—	—	
·00705	·000976	—	—	173·4	25	—	—	3915	—	—	—	—	—	—	
·0141	·00195	—	—	169·7	25	—	—	3832	—	—	—	—	—	—	[2] At 25°.

·0282	·0039	—	—	164·4	25	—	—	3712	—	—	—	—	—	—	
·0565	·0078	—	—	157·9	25	—	—	3565	—	—	—	—	—	—	
·113	·0156	—	—	148·7	25	—	—	3357	—	—	—	—	—	—	
·226	·0312	—	—	138·3	25	—	—	3122	—	—	—	—	—	—	
·452	·0625	—	—	127·0	25	—	—	2867	—	—	—	—	—	—	
—	·125	—	—	117·7	25	—	—	2658	—	—	—	—	—	—	
—	·25	—	—	109·9	25	—	—	2481	—	—	—	—	—	—	
—	·5	—	—	103·2	25	—	—	2330	—	—	—	—	—	—	
—	1·	—	—	97·3	25	—	—	2197	—	—	—	—	—	—	

Sodium Selenate.

Equivalent Gramme Molecule, $\frac{1}{2}Na_2SeO_4$, 94·44.

·0092	·000976	—	—	115·2[1]	25	—	—	1225[2]	—	—	—	—	—	—	
·0184	·00195	—	—	111·6	25	—	—	1186	—	—	—	—	—	—	
·0368	·0039	—	—	107·4	25	—	—	1126	—	—	—	—	—	—	
·0735	·0078	—	—	103·4	25	—	—	1099	—	—	—	—	—	—	
·147	·0156	—	—	98·1	25	—	—	1043	—	—	—	—	—	—	
·294	·0312	—	—	92·7	25	—	—	986	—	—	—	—	—	—	

[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 106.

[2] At 25°.

Phosphoric Acid.

Equivalent Gramme Molecule, $\frac{1}{3}H_3PO_4$, 32·67.

·0012	·000368	—	—	78·8[1]	25	—	—	1186	—	—	—	—	—	—	
·0024	·000735	—	—	79·8	25	—	—	1201	—	—	—	—	—	—	
·0048	·00147	—	—	79·0	25	—	—	1189	—	—	—	—	—	—	
·0096	·00295	—	—	75·4	25	—	—	1135	—	—	—	—	—	—	
·0192	·0059	—	—	69·9	25	—	—	1052	—	—	—	—	—	—	
·0385	·0118	—	—	61·8	25	—	—	931	—	—	—	—	—	—	
·077	·0235	—	—	53·1	25	—	—	799	—	—	—	—	—	—	
·154	·047	—	—	43·0	25	—	—	647	—	—	—	—	—	—	
·307	·094	—	—	34·4	25	—	—	518	—	—	—	—	—	—	
·598	·188	1·0029	15	27·1	25	—	—	408	—	—	·375	1057[2]	25	—	
1·215	·375	1·0076	15	21·3	25	—	—	321	—	—	·75	1026	25	—	
2·41	·75	1·0136	15	17·0	25	—	—	256	—	—	1·5	964	25	—	
4·76	1·5	1·0263	15	14·2	25	—	—	214	—	—	3·	849	25	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 460.

[2] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 750.

Potassium Carbonate.

Equivalent Gramme Molecule, $\frac{1}{2}K_2CO_3$, 69·13.

			°		°					°			°		
·000069	·00001	—	—	—	18	—	865[1]	919	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000138	·00002	—	—	—	18	—	882	938	—	—	—	—	—	—	
·000415	·00006	—	—	—	18	—	917	975	—	—	—	—	—	—	
·000691	·0001	—	—	—	18	—	995	1058	—	—	—	—	—	—	
·00138	·0002	—	—	—	18	—	1128	1199	—	—	—	—	—	—	[2] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
·00415	·0006	—	—	—	18	—	1222	1299	—	—	—	—	—	—	
·00691	·001	—	—	—	18	—	1221	1298	—	—	—	—	—	—	
·0138	·002	—	—	—	18	—	1199	1274	—	—	—	—	—	—	[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·0415	·006	—	—	—	18	—	1124	1195	—	—	—	—	—	—	
·0691	·01	—	—	—	18	·0249	1083	1151	—	—	—	—	—	—	
—	·029	—	—	—	—	—	—	—	·302[2]	—	—	—	—	—	
·207	·03	—	—	—	18	—	989	1051	—	—	—	—	—	—	[4] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·344	·05	1·0026	15	—	18	—	942	1001	—	—	—	—	—	—	
—	·074	—	—	—	—	—	—	—	·372	—	—	—	—	—	
·687	·1	1·0060	15	—	18	—	879	934	—	—	—	—	—	—	
—	·151	—	—	—	—	—	—	—	·377	—	—	—	—	—	
—	·441	—	—	—	—	—	—	—	·434	—	—	—	—	—	
3·354	·5	1·0306	15	—	18	·0227	728	774	—	—	—	—	—	—	
—	·764	—	—	—	—	—	—	—	·437	—	—	—	—	—	
6·522	1·	1·0600	15	—	18	·0219	660	702	·4	—	1·	809[3]	17·6	—	
—	1·607	—	—	—	—	—	—	—	·416	—	—	—	—	—	
12·39	2·	1·1162	15	—	18	·0211	584	620	—	—	—	—	—	—	
—	3·	—	—	—	18	·0210	517	550	—	—	—	—	—	—	
—	3·147	—	—	—	—	—	—	—	·404	—	—	—	—	—	
27·21	5·	1·2702	15	—	18	·0216	403	428	—	—	—	—	—	—	
—	8·112	—	—	—	—	—	—	—	·341	—	—	—	—	—	
46·14	10·	1·4959	15	—	18	·0285	169	180	—	—	—	—	—	—	
·407	·059	1·0032	15	52[4]	18	—	874	929	—	—	—	—	—	—	
·810	·118	1·0073	15	97	18	—	820	874	—	—	—	—	—	—	
1·608	·236	1·0147	15	181	18	—	767	815	—	—	—	—	—	—	
3·171	·472	1·0289	15	334	18	—	707	751	—	—	—	—	—	—	

Lithium Carbonate.

Equivalent Gramme Molecule, $\frac{1}{2}Li_2CO_3$, 37·02.

·00648	·00175	—	—	—	—	—	830[1]	882	—	—	—	—	—	—	[1] Vicentini, *Atti dell' Accad. di Torino*, vol. xx. p. 688.
·0111	·0030	—	—	—	—	—	790	840	—	—	—	—	—	—	
·0148	·0040	—	—	—	—	—	780	829	—	—	—	—	—	—	
·503	·136	—	—	—	—	—	—	—	·593[2]	—	—	—	—	—	[2] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
—	·232	—	—	—	—	—	—	—	·582	—	—	—	—	—	

Sodium Carbonate.

Equivalent Gramme Molecule, $\frac{1}{2}Na_2CO_3$, 53·04.

·000053	·00001	—	—	—	18	—	697[1]	740	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000106	·00002	—	—	—	18	—	715	760	—	—	—	—	—	—	
·000318	·00006	—	—	—	18	—	790	840	—	—	—	—	—	—	
·00053	·0001	—	—	—	18	—	874	929	—	—	—	—	—	—	
·00106	·0002	—	—	—	18	—	988	1050	—	—	—	—	—	—	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·00318	·0006	—	—	—	18	—	1046	1112	—	—	—	—	—	—	
·0053	·001	—	—	—	18	—	1037	1102	—	—	—	—	—	—	
·0106	·002	—	—	—	18	—	1010	1073	—	—	—	—	—	—	
·0318	·006	—	—	—	18	—	956	1016	—	—	—	—	—	—	[3] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
·053	·01	—	—	—	18	·0265	899	955	—	—	—	—	—	—	
·159	·03	—	—	—	18	—	799	850	—	—	—	—	—	—	
·264	·05	1·0019	15	—	18	—	751	798	—	—	—	—	—	—	
·5	·093	—	—	—	—	—	—	—	·474[3]	—	—	—	—	—	
·528	·1	1·0046	15	—	18	—	682	725	—	—	—	—	—	—	
—	·189	—	—	—	—	—	—	—	·519	—	—	—	—	—	
2·592	·5	1·0271	15	—	18	·0244	510	542	—	—	—	—	—	—	
5·0	·985	—	—	—	—	—	—	—	·548	—	—	—	—	—	
5·038	1·	1·0529	15	—	18	·0252	427	454	—	—	—	—	—	—	
—	2·844	—	—	—	—	—	—	—	·530	—	—	—	—	—	
13·86	3·	1·1479	15	—	18	·0289	254	270	—	—	—	—	—	—	
·659	·125	1·0060	15	79[2]	18	—	632	672	—	—	—	—	—	—	
1·307	·25	1·0137	15	142	18	—	568	603	—	—	—	—	—	—	
2·592	·5	1·0271	15	248	18	—	496	527	—	—	—	—	—	—	
5·038	1·	1·0529	15	433	18	—	433	460	—	—	—	—	—	—	

Potassium Chromate.

Equivalent Gramme Molecule, $\frac{1}{2}K_2CrO_4$, 97·33.

			°		°					°			°		
·638	·066	1·0044	19·5	60·1[1]	18	—	910	967	—	—	1·349[3]	882	20	—	[1] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
1·270	·132	1·0101	19·5	113·0	18	—	856	909	—	—	2·363	802	20	—	
2·515	·264	1·0203	19·5	212·0	18	—	803	853	—	—	4·407	620	20	—	
4·932	·528	1·0402	19·5	396·0	18	—	750	797	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 371.
9·80	—	—	—	—	—	—	—	—	·512[2]	—	—	—	—	—	[3] Sprung, *Pogg. Annal.* vol. clix. p. 1.

Ammonium Chromate.

Equivalent Gramme Molecule, $\frac{1}{2}(NH_4)_2CrO_4$, 76·24.

—	·0634	—	—	52[1]	18	—	820	871	—	—	—	—	—	—	[1] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	·1268	—	—	97	18	—	765	813	—	—	—	—	—	—	
—	·2536	—	—	177	18	—	698	742	—	—	—	—	—	—	
—	·517	—	—	318	18	—	615	653	—	—	—	—	—	—	

Potassium Bichromate.

Equivalent Gramme Molecule, $\frac{1}{2}K_2Cr_2O_7$, 147·52.

1·033	·0706	1·0073	19·5	62[1]	18	—	878	933	—	—	—	—	—	—	[1] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
2·050	·1413	1·0153	19·5	117	18	—	829	880	—	—	—	—	—	—	
4·040	·2826	1·0303	19·5	208	18	—	736	782	—	—	—	—	—	—	
6·390	—	—	—	—	—	—	—	—	·502[2]	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi. p. 371.
7·891	·5652	1·0553	19·5	415	18	—	734	780	—	—	—	—	—	—	

Ammonium Bichromate.

Equivalent Gramme Molecule, $\frac{1}{2}(NH_4)_2Cr_2O_7$, 126·44.

—	·0883	—	—	72·7[1]	18	—	823	874	—	—	—	—	—	—	[1] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	·1767	—	—	133·0	18	—	752	799	—	—	—	—	—	—	
—	·3534	—	—	252·0	18	—	713	757	—	—	—	—	—	—	
—	·7068	—	—	472·0	18	—	667	708	—	—	—	—	—	—	

Hydrocyanic Acid.

Equivalent Gramme Molecule, HCN, 26·98.

·084	·0312	—	—	·108[1]	25	—	—	4·882	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 304.
·168	·0625	—	—	·101	25	—	—	4·56	—	—	—	—	—	—	[2] At 25°.
·337	·125	—	—	·090	25	—	—	4·06	—	—	—	—	—	—	
·675	·25	—	—	·077	25	—	—	3·48	—	—	—	—	—	—	

Potassium Cyanide.

Equivalent Gramme Molecule, KCN, 65·02.

·946	—	—	—	—	—	—	—	—	·47[2]	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 149.
3·20	·5	1·0154	15	488[1]	18	·0208	976	1037	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cvi.
6·30	1·	1·0312	15	938	18	·0195	938	997	—	—	—	—	—	—	
11·55	—	—	—	—	—	—	—	—	·457	—	—	—	—	—	

Sulphocyanic Acid.

Equivalent Gramme Molecule, HCNS, 58·96.

·00145	·000244	—	—	84·1[1]	25	—	—	3797[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 305.
·0029	·000488	—	—	85·8	25	—	—	3874	—	—	—	—	—	—	
·0058	·000976	—	—	86·3	25	—	—	3897	—	—	—	—	—	—	[2] At 25°.
·0115	·00195	—	—	86·8	25	—	—	3919	—	—	—	—	—	—	
·023	·0039	—	—	86·5	25	—	—	3905	—	—	—	—	—	—	
·046	·0078	—	—	86·5	25	—	—	3905	—	—	—	—	—	—	
·092	·0156	—	—	85·2	25	—	—	3847	—	—	—	—	—	—	
·184	·0312	—	—	84·2	25	—	—	3802	—	—	—	—	—	—	
—	·0625	—	—	82·8	25	—	—	3739	—	—	—	—	—	—	
—	·125	—	—	81·2	25	—	—	3666	—	—	—	—	—	—	
—	·25	—	—	79·3	25	—	—	3581	—	—	—	—	—	—	
—	·5	—	—	76·7	25	—	—	3463	—	—	—	—	—	—	

Hydroferrocyanic Acid.

Equivalent Gramme Molecule, $\frac{1}{4}H_4FeCy_6$, 53·95.

·00131	·000244	—	—	80·4[1]	25	—	—	3630[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 307.
·00262	·000488	—	—	76·2	25	—	—	3440	—	—	—	—	—	—	
·00525	·000976	—	—	72·0	25	—	—	3251	—	—	—	—	—	—	[2] At 25°.
·0105	·00195	—	—	67·1	25	—	—	3030	—	—	—	—	—	—	
·0210	·0039	—	—	62·7	25	—	—	2831	—	—	—	—	—	—	
·0421	·0078	—	—	58·6	25	—	—	2646	—	—	—	—	—	—	
·0841	·0156	—	—	55·1	25	—	—	2488	—	—	—	—	—	—	

Formic Acid.

Equivalent Gramme Molecule, HCOOH, 46.

			°		°				°			°		
·00225	·000488	—	—	36·00[1]	25	—	—	1622[2]	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 445.
·0045	·000976	—	—	29·04	25	—	—	1311	—	—	—	—	—	
·0090	·00195	—	—	22·54	25	—	—	1018	—	—	—	—	—	
·0180	·0039	—	—	17·00	25	—	—	768	—	—	—	—	—	[2] At 25°.
·0359	·0078	—	—	12·58	25	—	—	568	—	—	—	—	—	
·0718	·0156	—	—	9·18	25	—	—	414	—	—	—	—	—	
·1435	·0312	—	—	6·63	25	—	—	299	—	—	—	—	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·287	·0625	—	—	4·79	25	—	—	217	—	—	·125[3]	1087	25	—
·574	·125	1·0015	25	3·43	25	—	—	155	—	—	·25	1083	25	—
—	·25	1·0030	25	2·46	25	—	—	111	—	—	·5	1075	25	—
—	·5	1·0058	25	1·76	25	—	—	79	—	—	1·0	1060	25	—
														[4] Berthelot, *Annales de Chimie*, series 6, vol. xxiii. p. 39.
·0046	·001	—	—	103[4]	17	—	—	1405	—	—	—	—	—	—
·0092	·002	—	—	77·8	17	—	—	1061	—	—	—	—	—	—
·046	·01	—	—	38·4	17	·018	—	524	—	—	—	—	—	—
·115	·025	—	—	24·9	17	—	—	340	—	—	—	—	—	—
·23	·05	—	—	17·9	17	—	—	245	—	—	—	—	—	—
·46	·1	—	—	12·9	17	—	—	176	—	—	—	—	—	—

Potassium Formate.

Equivalent Gramme Molecule, HCOOK, 84·13.

·0082	·000976	—	—	120·1[1]	25	—	—	1277[3]	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 102.
·0164	·00195	—	—	117·3	25	—	—	1247	—	—	—	—	—	
·0328	·0039	—	—	114·7	25	—	—	1219	—	—	—	—	—	
·0655	·0078	—	—	112·3	25	—	—	1194	—	—	—	—	—	
·131	·0156	—	—	108·8	25	—	—	1156	—	—	—	—	—	[2] Berthelot, *Annales de Chimie*, vol. xxiii. p. 40.
·262	·0312	—	—	105·8	25	—	—	1124	—	—	—	—	—	
·0042	·0005	—	—	95[2]	17	—	—	1341	—	—	—	—	—	[3] At 25°.
·0168	·002	—	—	91·5	17	—	—	1291	—	—	—	—	—	
·042	·005	—	—	87·6	17	·023	—	1236	—	—	—	—	—	

Sodium Formate.

Equivalent Gramme Molecule, HCOONa, 68·04.

·0066	·000976	—	—	98·9[1]	25	—	—	1051[2]	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 99.
·0132	·00195	—	—	96·9	25	—	—	1030	—	—	—	—	—	
·0265	·0039	—	—	94·7	25	—	—	1007	—	—	·125[3]	1068	25	—

·053	·0078	—	—	92·0	25	—	—	978	—	—	·25	1046	25	—	[2] At 25°.
·106	·0156	—	—	89·0	25	—	—	946	—	—	·5	998	25	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 750.
·212	·0312	—	—	85·8	25	—	—	912	—	—	1·0	906	25	—	

Lithium Formate.

Equivalent Gramme Molecule, HCOOLi, 52·02.

·00505	·000976	—	—	88·1[1]	25	—	—	936[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 103.
·0101	·00195	—	—	85·8	25	—	—	912	—	—	—	—	—	—	
·0202	·0039	—	—	83·4	25	—	—	886	—	—	—	—	—	—	
·0405	·0078	—	—	80·8	25	—	—	859	—	—	—	—	—	—	[2] At 25°.
·081	·0156	—	—	77·9	25	—	—	828	—	—	—	—	—	—	
·162	·0312	—	—	75·0	25	—	—	797	—	—	—	—	—	—	

Acetic Acid.

Equivalent Gramme Molecule, CH_3COOH, 60.

·00146	·000244	—	—	19·37[1]	25	—	—	785	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 444.
·00292	·000488	—	—	14·48	25	—	—	586	—	—	—	—	—	—	
·00585	·000976	—	—	10·48	25	—	—	424	—	—	—	—	—	—	
·0117	·00195	—	—	7·77	25	—	—	314	—	—	—	—	—	—	[2] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·0234	·0039	—	—	5·66	25	—	—	229	—	—	—	—	—	—	
·0468	·0078	—	—	4·08	25	—	—	166	—	—	—	—	—	—	
·0935	·0156	—	—	2·94	25	—	—	119	—	—	—	—	—	—	
·187	·0312	—	—	2·123	25	—	—	86·1	—	—	—	—	—	—	[3] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 197.
·374	·0625	—	—	1·514	25	—	—	61·4	—	—	—	—	—	—	
·748	·125	1·0003	15	1·078	25	—	—	43·7	—	—	·125	1074[2]	25	—	
1·494	·25	1·0014	15	·756	25	—	—	30·6	—	—	·25	1060	25	—	
2·982	·5	1·0036	15	·520	25	—	—	21·1	—	—	·5	1031	25	—	
—	—	—	—	—	—	—	—	—	—	—	1·0	982	25	—	
·00006	·00001	—	—	—	18	—	1304[3]	1386	—	—	—	—	—	—	
·00012	·00002	—	—	—	18	—	1328	1412	—	—	—	—	—	—	
·00036	·00006	—	—	—	18	—	1133	1204	—	—	—	—	—	—	
·0006	·0001	—	—	—	18	—	995	1058	—	—	—	—	—	—	
·0012	·0002	—	—	—	18	—	796	846	—	—	—	—	—	—	
·0036	·0006	—	—	—	18	—	470	500	—	—	—	—	—	—	
·006	·001	—	—	—	18	—	380	404	—	—	—	—	—	—	
·012	·002	—	—	—	18	—	283	301	—	—	—	—	—	—	
·036	·006	—	—	—	18	—	170	181	—	—	—	—	—	—	
·06	·01	—	—	—	18	—	132	140	—	—	—	—	—	—	

Acetic Acid—*continued.*

Equivalent Gramme Molecule, CH_3COOH, 60.

			°		°					°				°	
·18	·03	—	—	—	18	—	79	84	—	—	—	—	—	—	[4] Berthelot, *Annales de Chimie*, vol. xxiii. p. 43.
·30	·05	—	—	—	18	—	62	66	—	—	—	—	—	—	
·60	·1	1·0002	15	—	18	—	43	46	—	—	—	—	—	—	
2·98	·5	1·0036	15	—	18	—	19	20·2	—	—	—	—	—	—	
5·95	1·	1·0080	15	—	18	—	12	12·7	—	—	—	—	—	—	
17·56	3·	1·0246	15	—	18	—	5·2	5·5	—	—	—	—	—	—	
28·87	5·	1·0389	15	—	18	—	2·6	2·8	—	—	—	—	—	—	
56·39	10·	1·0644	15	—	18	—	·5	·53	—	—	—	—	—	—	
·006	·001	—	—	35·0[4]	17	—	—	425	—	—	—	—	—	—	
·012	·002	—	—	25·2	17	—	—	306	—	—	—	—	—	—	
·030	·005	—	—	16·2	17	—	—	196	—	—	—	—	—	—	
·060	·01	—	—	11·6	17	·018	—	141	—	—	—	—	—	—	

Potassium Acetate.

Equivalent Gramme Molecule, CH_3COOK, 98·13.

·000098	·00001	—	—	—	18	—	939[1]	998	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 195.
·000196	·00002	—	—	—	18	—	943	1002	—	—	—	—	—	—	
·000588	·00006	—	—	—	18	—	935	994	—	—	—	—	—	—	
·00098	·0001	—	—	—	18	—	934	993	—	—	—	—	—	—	[2] Hittorf, *Pogg. Annal.* vol. cii. p. 42.
·00196	·0002	—	—	—	18	—	933	992	—	—	—	—	—	—	
·00588	·0006	—	—	—	18	—	923	981	—	—	—	—	—	—	
·0098	·001	—	—	—	18	—	919	977	—	—	—	—	—	—	[3] Arrhenius, *Zeitschrift für physik. Chemie*, vol. i. p. 295.
·0196	·002	—	—	—	18	—	913	970	—	—	—	—	—	—	
·0588	·006	—	—	—	18	—	891	947	—	—	—	—	—	—	
·098	·01	—	—	—	18	·0229	879	934	—	—	—	—	—	—	
·294	·03	—	—	—	18	—	841	894	—	—	1·	735[3]	17·6	—	
—	·05	—	—	—	18	—	820	872	—	—	—	—	—	—	
—	·1	—	—	—	18	—	784	833	—	—	—	—	—	—	
1·057	·114	1·0051	14	—	—	—	—	—	·324[2]	—	—	—	—	—	
—	·5	—	—	—	18	·0224	671	713	—	—	—	—	—	—	
9·37	1·	1·0467	18·6	—	18	·0220	594	631	—	—	—	—	—	—	
—	3·	—	—	—	18	·0227	381	405	—	—	—	—	—	—	
—	5·	—	—	—	18	·0252	240	255	—	—	—	—	—	—	
42·7	5·4	1·2396	11	—	—	—	—	—	·325	—	—	—	—	—	
—	10·	—	—	—	18	·0421	30	32	—	—	—	—	—	—	

·0095	·000976	—	—	105·1[4]	25	—	—	943	—	—	—	—	—	—	[4] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 102.
·0191	·00195	—	—	103·1	25	—	—	934	—	—	—	—	—	—	
·0382	·0039	—	—	100·4	25	—	—	915	—	—	—	—	—	—	
·0765	·0078	—	—	98·2	25	—	—	900	—	—	—	—	—	—	[5] Berthelot, *Annales de Chimie*, vol. xxiii. p. 43.
·153	·0156	—	—	95·4	25	—	—	874	—	—	—	—	—	—	
·306	·0312	—	—	92·9	25	—	—	851	—	—	—	—	—	—	
·0049	·0005	—	—	83·6[5]	17	—	—	1019	—	—	—	—	—	—	
·0196	·002	—	—	80·5	17	—	—	982	—	—	—	—	—	—	
·0294	·0033	—	—	78·0	17	—	—	951	—	—	—	—	—	—	
·049	·005	—	—	77·2	17	—	—	942	—	—	—	—	—	—	
·059	·0066	—	—	76·5	17	—	—	933	—	—	—	—	—	—	
·098	·01	—	—	75·4	17	—	—	920	—	—	—	—	—	—	

Sodium Acetate.

Equivalent Gramme Molecule, CH_3COONa, 82·04.

1·17	·142	1·0062	11	—	—	—	—	—	·443[3]	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 150.
2·36	·288	1·0125	5·5	—	—	—	—	—	·424	—	—	—	—	—	
—	·5	—	—	233[1]	18	·0253	466	495	—	—	—	—	—	—	
—	1·	—	—	389	18	·0255	389	413	—	—	·125	1047[4]	25	—	
12·22	1·6	1·0661	13	—	—	—	—	—	·421	—	·25	1003	25	—	[2] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 99.
—	2·	—	—	561	18	·0275	280	297	—	—	·5	926	25	—	
—	3·	—	—	609	18	·0306	203	215	—	—	1·	785	25	—	
26·26	3·64	1·1455	7·7	—	—	—	—	—	·415	—	—	—	—	—	
—	4·	—	—	575	18	·0340	119	126	—	—	—	—	—	—	[3] Hittorf, *Pogg. Annal.* vol. cvi. p. 379.
—	5·	—	—	495	18	·0410	99	105	—	—	—	—	—	—	
·008	·000976	—	—	84·9[2]	25	—	—	768	—	—	—	—	—	—	
·016	·00195	—	—	83·3	25	—	—	754	—	—	—	—	—	—	[4] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 750.
·032	·0039	—	—	81·2	25	—	—	735	—	—	—	—	—	—	
·064	·0078	—	—	79·0	25	—	—	715	—	—	—	—	—	—	
·128	·0156	—	—	76·4	25	—	—	691	—	—	—	—	—	—	
·256	·0312	—	—	73·6	25	—	—	666	—	—	—	—	—	—	

Monochloracetic Acid.

Equivalent Gramme Molecule, $CH_2ClCOOH$, 94·46.

·0023	·000244	—	—	68·69[1]	25	—	—	3102[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 446.
·0046	·000488	—	—	63·48	25	—	—	2866	—	—	—	—	—	—	
·0092	·000976	—	—	55·64	25	—	—	2512	—	—	—	—	—	—	[2] At 25°.
·0184	·00195	—	—	46·75	25	—	—	2111	—	—	—	—	—	—	

Monochloracetic Acid—*continued.*

Equivalent Gramme Molecule, $CH_2ClCOOH$, 94·46.

			°		°					°			°		
·0368	·0039	—	—	37·81	25	—	—	1707	—	—	—	—	—	—	
·0735	·0078	—	—	29·61	25	—	—	1337	—	—	—	—	—	—	
·147	·0156	—	—	22·85	25	—	—	1032	—	—	—	—	—	—	
·294	·0312	—	—	17·29	25	—	—	781	—	—	—	—	—	—	
·588	·0625	—	—	12·86	25	—	—	578	—	—	—	—	—	—	
—	·125	—	—	9·53	25	—	—	430	—	—	—	—	—	—	
—	·25	—	—	6·98	25	—	—	316	—	—	—	—	—	—	
—	·5	—	—	4·99	25	—	—	179	—	—	—	—	—	—	

Dichloracetic Acid.

Equivalent Gramme Molecule, $CHCl_2COOH$, 128·92.

·00312	·000244	—	—	79·28[1]	25	—	—	3600[2]	—	—	—	—	—	—	
·00625	·000488	—	—	80·94	25	—	—	3651	—	—	—	—	—	—	
·0125	·000976	—	—	80·48	25	—	—	3636	—	—	—	—	—	—	
·025	·00195	—	—	79·70	25	—	—	3601	—	—	—	—	—	—	
·050	·0039	—	—	76·30	25	—	—	3442	—	—	—	—	—	—	
·100	·0078	—	—	72·52	25	—	—	3271	—	—	—	—	—	—	
·200	·0156	—	—	67·56	25	—	—	3043	—	—	—	—	—	—	
·400	·0312	—	—	60·30	25	—	—	2720	—	—	—	—	—	—	
·800	·0625	—	—	52·08	25	—	—	2356	—	—	—	—	—	—	
—	·125	—	—	43·03	25	—	—	1912	—	—	—	—	—	—	
—	·25	—	—	34·42	25	—	—	1550	—	—	—	—	—	—	
—	·5	—	—	25·75	25	—	—	1161	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 446.

[2] At 25°.

Trichloracetic Acid.

Equivalent Gramme Molecule, $CCl_3CO{\cdot}OH$, 163·38.

·00398	·000244	—	—	77·84[1]	25	—	—	3515[2]	—	—	—	—	—	—	
·00795	·000488	—	—	79·10	25	—	—	3572	—	—	—	—	—	—	
·0159	·000976	—	—	79·68	25	—	—	3598	—	—	—	—	—	—	
·0318	·00195	—	—	79·58	25	—	—	3593	—	—	—	—	—	—	
·0635	·0039	—	—	79·12	25	—	—	3572	—	—	—	—	—	—	
·127	·0078	—	—	79·00	25	—	—	3567	—	—	—	—	—	—	
·254	·0156	—	—	78·55	25	—	—	3547	—	—	—	—	—	—	
·508	·0312	—	—	76·95	25	—	—	3475	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 322.

[2] At 25°.

—	·0625	—	—	74·62	25	—	—	3369	—	—	—	—	—	—	
—	·125	—	—	71·14	25	—	—	3212	—	—	—	—	—	—	
—	·25	—	—	65·63	25	—	—	2963	—	—	—	—	—	—	
—	·5	—	—	57·56	25	—	—	2599	—	—	—	—	—	—	

Monobromacetic Acid.

Equivalent Gramme Molecule, $CH_2BrCOOH$, 138·95.

·00338	·000244	—	—	69·97[1]	25	—	—	3159[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 322.
·00675	·000488	—	—	64·02	25	—	—	2891	—	—	—	—	—	—	
·0135	·000976	—	—	55·47	25	—	—	2505	—	—	—	—	—	—	
·027	·00195	—	—	46·14	25	—	—	2083	—	—	—	—	—	—	[2] At 25°.
·054	·0039	—	—	36·83	25	—	—	1663	—	—	—	—	—	—	
·108	·0078	—	—	28·52	25	—	—	1288	—	—	—	—	—	—	
·216	·0156	—	—	21·62	25	—	—	976	—	—	—	—	—	—	
·432	·0312	—	—	16·12	25	—	—	728	—	—	—	—	—	—	
·863	·0625	—	—	11·90	25	—	—	537	—	—	—	—	—	—	
—	·125	—	—	8·65	25	—	—	391	—	—	—	—	—	—	

Potassium Trichloracetate.

Equivalent Gramme Molecule, CCl_3COOK, 201·51.

·0196	·000976	—	—	101·9[1]	25	—	—	1083[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 103.
·0392	·00195	—	—	99·5	25	—	—	1058	—	—	—	—	—	—	
·0785	·0039	—	—	96·8	25	—	—	1029	—	—	—	—	—	—	
·157	·0078	—	—	94·3	25	—	—	1002	—	—	—	—	—	—	[2] At 25°.
·314	·0156	—	—	91·7	25	—	—	975	—	—	—	—	—	—	
·628	·0312	—	—	88·5	25	—	—	941	—	—	—	—	—	—	

Sodium Trichloracetate.

Equivalent Gramme Molecule, CCl_3COONa, 185·42.

·018	·000976	—	—	80·7[1]	25	—	—	856[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 100.
·036	·00195	—	—	78·7	25	—	—	837	—	—	—	—	—	—	
·072	·0039	—	—	76·8	25	—	—	816	—	—	—	—	—	—	
·144	·0078	—	—	74·8	25	—	—	795	—	—	—	—	—	—	[2] At 25°.
·288	·0156	—	—	72·6	25	—	—	772	—	—	—	—	—	—	
·576	·0312	—	—	70·0	25	—	—	744	—	—	—	—	—	—	

Lithium Trichloracetate.

Equivalent Gramme Molecule, CCl_3COOLi, 169·4.

			°		°				°				°		
·0165	·000976	—	—	70·2[1]	25	—	—	746[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 104.
·033	·00195	—	—	68·1	25	—	—	724	—	—	—	—	—	—	
·066	·0039	—	—	66·0	25	—	—	702	—	—	—	—	—	—	
·132	·0078	—	—	64·2	25	—	—	682	—	—	—	—	—	—	
·264	·0156	—	—	62·0	25	—	—	659	—	—	—	—	—	—	[2] At 25°.
·528	·0312	—	—	59·9	25	—	—	637	—	—	—	—	—	—	

Propionic Acid.

Equivalent Gramme Molecule, C_2H_5COOH, 74.

·0018	·000244	—	—	18·2[1]	25	—	—	822[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 317.
·0036	·000448	—	—	13·19	25	—	—	596	—	—	—	—	—	—	
·0072	·000976	—	—	9·56	25	—	—	432	—	—	—	—	—	—	
·0144	·00195	—	—	6·88	25	—	—	310	—	—	—	—	—	—	
·0289	·0039	—	—	4·92	25	—	—	222	—	—	—	—	—	—	[2] At 25°.
·0578	·0078	—	—	3·50	25	—	—	158	—	—	—	—	—	—	
·1155	·0156	—	—	2·49	25	—	—	112	—	—	—	—	—	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·231	·0312	—	—	1·767	25	—	—	80	—	—	—	—	—	—	
·462	·0625	—	—	1·247	25	—	—	56	—	—	·125	1065[3]	25	—	
·924	·125	1·0011	25	·871	25	—	—	39	—	—	·25	1044	25	—	
1·846	·25	1·0019	25	·601	25	—	—	27	—	—	·5	994	25	—	
3·687	·5	1·0035	25	·403	25	—	—	18	—	—	1·	913	25	—	

Potassium Propionate.

Equivalent Gramme Molecule, C_2H_5COOK, 112·13.

·0110	·000976	—	—	103·0[1]	25	—	—	1095[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 102.
·0219	·00195	—	—	101·1	25	—	—	1064	—	—	—	—	—	—	
·0438	·0039	—	—	97·4	25	—	—	1035	—	—	—	—	—	—	
·0875	·0078	—	—	94·9	25	—	—	1009	—	—	—	—	—	—	
·175	·0156	—	—	92·1	25	—	—	979	—	—	—	—	—	—	[2] At 25°.
·350	·0312	—	—	89·0	25	—	—	946	—	—	—	—	—	—	

Sodium Propionate.

Equivalent Gramme Molecule, C_2H_5COONa, 96·04.

·0094	·000976	—	—	80·4[1]	25	—	—	854[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 99.
·0188	·00195	—	—	78·8	25	—	—	837	—	—	·125	1036[3]	25	—	
·0375	·0039	—	—	76·5	25	—	—	813	—	—	·25	983	25	—	
·075	·0078	—	—	74·5	25	—	—	792	—	—	·5	885	25	—	[2] At 25°.
·150	·0156	—	—	71·9	25	—	—	764	—	—	1·	711	25	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 750.
·300	·0312	—	—	69·4	25	—	—	737	—	—	—	—	—	—	

Lithium Propionate.

Equivalent Gramme Molecule, C_2H_5COOLi, 80·02.

·0078	·00976	—	—	69·5[1]	25	—	—	739[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 104.
·0156	·00195	—	—	67·5	25	—	—	717	—	—	—	—	—	—	
·0312	·0039	—	—	65·5	25	—	—	696	—	—	—	—	—	—	
·0625	·0078	—	—	63·5	25	—	—	675	—	—	—	—	—	—	[2] At 25°.
·125	·0156	—	—	60·6	25	—	—	644	—	—	—	—	—	—	
·250	·0312	—	—	57·9	25	—	—	615	—	—	—	—	—	—	

A. Brompropionic Acid.

Equivalent Gramme Molecule, $C_2H_4BrCOOH$, 152·95.

·00372	·000244	—	—	68·9[1]	—	—	—	3111[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 324.
·00745	·000488	—	—	62·2	—	—	—	2807	—	—	—	—	—	—	
·0149	·000976	—	—	53·7	—	—	—	2423	—	—	—	—	—	—	
·0298	·00195	—	—	44·7	—	—	—	2020	—	—	—	—	—	—	[2] At 25°.
·0595	·0039	—	—	36·1	—	—	—	1632	—	—	—	—	—	—	
·119	·0078	—	—	28·8	—	—	—	1299	—	—	—	—	—	—	
·238	·0156	—	—	22·6	—	—	—	1020	—	—	—	—	—	—	
·477	·0312	—	—	17·6	—	—	—	796	—	—	—	—	—	—	
—	·0625	—	—	13·7	—	—	—	619	—	—	—	—	—	—	
—	·125	—	—	10·5	—	—	—	475	—	—	—	—	—	—	
—	·25	—	—	7·9	—	—	—	355	—	—	—	—	—	—	
—	·5	—	—	5·6	—	—	—	252	—	—	—	—	—	—	

B. Iodopropionic Acid.

Equivalent Gramme Molecule, CH_2ICH_2COOH, 199·8.

			°		°					°				°	
·0049	·000244	—	—	36·0[1]	25	—	—	162·8[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 325.
·0098	·000488	—	—	28·2	25	—	—	127·2	—	—	—	—	—	—	
·0195	·000976	—	—	21·3	25	—	—	96·4	—	—	—	—	—	—	
·039	·00195	—	—	15·8	25	—	—	71·5	—	—	—	—	—	—	[2] At 25°.
·078	·0039	—	—	11·6	25	—	—	52·4	—	—	—	—	—	—	
·156	·0078	—	—	8·45	25	—	—	38·1	—	—	—	—	—	—	
·312	·0156	—	—	6·10	25	—	—	27·5	—	—	—	—	—	—	
·624	·0312	—	—	4·38	25	—	—	19·8	—	—	—	—	—	—	
—	·0625	—	—	3·12	25	—	—	14·1	—	—	—	—	—	—	
—	·125	—	—	2·22	25	—	—	10·0	—	—	—	—	—	—	
—	·25	—	—	1·53	25	—	—	6·9	—	—	—	—	—	—	

Butyric Acid.

Equivalent Gramme Molecule, C_3H_7COOH, 88.

·00214	·000244	—	—	18·0[1]	25	—	—	81·4[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 444.
·00428	·000488	—	—	13·4	25	—	—	60·4	—	—	—	—	—	—	
·00855	·000976	—	—	9·74	25	—	—	44·0	—	—	—	—	—	—	
·0171	·00195	—	—	7·01	25	—	—	31·7	—	—	—	—	—	—	
·0342	·0039	—	—	5·04	25	—	—	22·8	—	—	—	—	—	—	[2] At 25°.
·0685	·0078	—	—	3·59	25	—	—	16·2	—	—	—	—	—	—	
·137	·0156	—	—	2·56	25	—	—	11·6	—	—	—	—	—	—	
·274	·0312	—	—	1·81	25	—	—	8·2	—	—	—	—	—	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·548	·0625	—	—	1·27	25	—	—	5·8	—	—	·125	1060[3]	25	—	
1·099	·125	1·0006	25	·88	25	—	—	4·0	—	—	·25	1027	25	—	
2·197	·25	1·0013	25	·60	25	—	—	2·7	—	—	·5	966	25	—	
4·390	·5	1·0022	25	·39	25	—	—	1·8	—	—	1·	854	25	—	

Potassium Butyrate.

Equivalent Gramme Molecule, C_3H_7COOK, 126·13.

·0122	·000976	—	—	100·3[1]	25	—	—	106·6[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 102.
·0245	·00195	—	—	97·4	25	—	—	103·5	—	—	—	—	—	—	
·049	·0039	—	—	94·8	25	—	—	100·8	—	—	—	—	—	—	
·098	·0078	—	—	92·5	25	—	—	98·3	—	—	—	—	—	—	
·196	·0156	—	—	89·0	25	—	—	94·6	—	—	—	—	—	—	[2] At 25°.
·393	·0312	—	—	86·3	25	—	—	91·7	—	—	—	—	—	—	

Sodium Butyrate.

Equivalent Gramme Molecule, C_3H_7COONa, 110·04.

·0108	·000976	—	—	76·4[1]	25	—	—	812[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 99.
·0215	·00195	—	—	75·0	25	—	—	797	—	—	·125	1025[3]	25	—	
·043	·0039	—	—	73·4	25	—	—	780	—	—	·25	962	25	—	[2] At 25°.
·086	·0078	—	—	71·2	25	—	—	757	—	—	·5	845	25	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 751.
·172	·0156	—	—	68·9	25	—	—	732	—	—	1·	652	25	—	
·343	·0312	—	—	66·2	25	—	—	703	—	—	—	—	—	—	

Lithium Butyrate.

Equivalent Gramme Molecule, C_3H_7COOLi, 94·02.

·0091	·000976	—	—	66·5[1]	25	—	—	707[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 104.
·0182	·00195	—	—	64·7	25	—	—	688	—	—	—	—	—	—	
·0365	·0039	—	—	63·0	25	—	—	670	—	—	—	—	—	—	[2] At 25°.
·073	·0078	—	—	60·8	25	—	—	646	—	—	—	—	—	—	
·146	·0156	—	—	58·2	25	—	—	619	—	—	—	—	—	—	
·293	·0312	—	—	55·5	25	—	—	590	—	—	—	—	—	—	

Isobutyric Acid.

Equivalent Gramme Molecule, C_3H_7COOH, 88.

·00215	·000244	—	—	17·62[1]	25	—	—	797[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 318.
·0043	·000488	—	—	12·97	25	—	—	587	—	—	—	—	—	—	
·0086	·000976	—	—	9·50	25	—	—	430	—	—	—	—	—	—	[2] At 25°.
·0172	·00195	—	—	6·86	25	—	—	310	—	—	—	—	—	—	
·0345	·0039	—	—	4·95	25	—	—	224	—	—	—	—	—	—	
·069	·0078	—	—	3·55	25	—	—	161	—	—	—	—	—	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·138	·0156	—	—	2·54	25	—	—	115	—	—	—	—	—	—	
·275	·0312	—	—	1·81	25	—	—	82	—	—	—	—	—	—	
·550	·0625	—	—	1·27	25	—	—	57	—	—	·125[3]	1059	25	—	
1·100	·125	1·0004	25	·89	25	—	—	40	—	—	·25	1025	25	—	
2·198	·25	1·0008	25	·61	25	—	—	27·6	—	—	·5	968	25	—	
4·392	·5	1·0016	25	·39	25	—	—	17·6	—	—	1·	859	25	—	

Potassium Isobutyrate.

Equivalent Gramme Molecule, C_3H_7COOK, 126·13.

·0122	·000976	—	—	100·2[1]	25	—	—	1065[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 102.
·0245	·00195	—	—	97·4	25	—	—	1035	—	—	—	—	—	—	
·049	·0039	—	—	94·9	25	—	—	1009	—	—	—	—	—	—	
·098	·0078	—	—	92·5	25	—	—	983	—	—	—	—	—	—	
·196	·0156	—	—	89·6	25	—	—	952	—	—	—	—	—	—	[2] At 25°.
·393	·0312	—	—	86·7	25	—	—	922	—	—	—	—	—	—	

Sodium Isobutyrate.

Equivalent Gramme Molecule, C_3H_7COONa, 110·04.

·0108	·000976	—	—	79·0[1]	25	—	—	840[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 99.
·0215	·00195	—	—	76·6	25	—	—	814	—	—	·125[3]	1021	25	—	
·043	·0039	—	—	74·3	25	—	—	790	—	—	·25	956	25	—	
·086	·0078	—	—	71·6	25	—	—	761	—	—	·5	841	25	—	[2] At 25°.
·172	·0156	—	—	68·9	25	—	—	732	—	—	1·	649	25	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 751.
·343	·0312	—	—	66·0	25	—	—	701	—	—	—	—	—	—	

Lithium Isobutyrate.

Equivalent Gramme Molecule, C_3H_7COOLi, 94·02.

·0091	·000976	—	—	66·5[1]	25	—	—	707[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 104.
·0182	·00195	—	—	64·8	25	—	—	689	—	—	—	—	—	—	
·0365	·0039	—	—	63·0	25	—	—	670	—	—	—	—	—	—	
·073	·0078	—	—	60·7	25	—	—	645	—	—	—	—	—	—	
·146	·0156	—	—	58·4	25	—	—	621	—	—	—	—	—	—	[2] At 25°.
·293	·0312	—	—	55·6	25	—	—	591	—	—	—	—	—	—	

Lactic Acid.

Equivalent Gramme Molecule, $CH_3C(OH)HCOOH$, 90.

·0022	·000244	—	—	44·0[1]	25	—	—	1987[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 328.
·0044	·000488	—	—	33·8	25	—	—	1526	—	—	—	—	—	—	
·0088	·000976	—	—	26·0	25	—	—	1174	—	—	—	—	—	—	
·0175	·00195	—	—	19·5	25	—	—	881	—	—	—	—	—	—	
·035	·0039	—	—	14·4	25	—	—	650	—	—	—	—	—	—	[2] At 25°.
·070	·0078	—	—	10·6	25	—	—	479	—	—	—	—	—	—	

·140	·0156	—	—	7·6	25	—	—	343	—	—	—	—	—	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 749.
·280	·0312	—	—	5·5	25	—	—	248	—	—	—	—	—	—	
·560	·0625	—	—	3·9	25	—	—	177	—	—	·125[3]	1059	25	—	
1·122	·125	1·0026	25	2·8	25	—	—	125	—	—	·25	1032	25	—	
2·239	·25	1·0052	25	1·9	25	—	—	88	—	—	·5	976	25	—	
4·455	·5	1·0103	25	1·3	25	—	—	60	—	—	1·	874	25	—	

Potassium Lactate.

Equivalent Gramme Molecule, $CH_3C(OH)HCOOK$, 128·13.

·0125	·000976	—	—	102·6[1]	25	—	—	1091[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 103.
·025	·00195	—	—	99·9	25	—	—	1062	—	—	—	—	—	—	
·050	·0039	—	—	97·5	25	—	—	1036	—	—	—	—	—	—	
·100	·0078	—	—	94·8	25	—	—	1008	—	—	—	—	—	—	[2] At 25°.
·200	·0156	—	—	91·9	25	—	—	977	—	—	—	—	—	—	
·400	·0312	—	—	88·9	25	—	—	945	—	—	—	—	—	—	

Sodium Lactate.

Equivalent Gramme Molecule, $CH_3C(OH)HCOONa$, 112·04.

·0110	·000976	—	—	81·1[1]	25	—	—	862[2]	—	—	—	—	—	—	[1] Ostwald, *Zeitschrift für physik. Chemie*, vol. i. p. 100.
·0219	·00195	—	—	79·2	25	—	—	842	—	—	·125[3]	1039	25	—	
·0438	·0039	—	—	77·1	25	—	—	820	—	—	·25	990	25	—	[2] At 25°.
·0875	·0078	—	—	74·6	25	—	—	793	—	—	·5	893	25	—	
·175	·0156	—	—	71·9	25	—	—	764	—	—	1·	729	25	—	[3] Reyher, *Zeitschrift für physik. Chemie*, vol. ii. p. 751.
·349	·0312	—	—	69·4	25	—	—	738	—	—	—	—	—	—	

Oxalic Acid.

Equivalent Gramme Molecule, $\frac{1}{2}(COOH)_2$, 45.

·0011	·000244	—	—	59·2[1]	25	—	—	2434	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxi. p. 457.
·0022	·000488	—	—	49·3	25	—	—	2027	—	—	—	—	—	—	
·0044	·000976	—	—	46·0	25	—	—	1889	—	—	—	—	—	—	
·0088	·00195	—	—	43·6	25	—	—	1792	—	—	—	—	—	—	
·0175	·0039	—	—	41·8	25	—	—	1717	—	—	—	—	—	—	
·035	·0078	—	—	39·9	25	—	—	1638	—	—	—	—	—	—	
·070	·0156	—	—	37·5	25	—	—	1542	—	—	—	—	—	—	
·140	·0312	—	—	34·5	25	—	—	1417	—	—	—	—	—	—	

Oxalic Acid—*continued.*

Equivalent Gramme Molecule, $\frac{1}{2}(COOH)_2$, 45.

			°		°					°				°		
·280	·0625	—	—	30·7	25	—	—	1261	—	—	—	—	—	—	
·560	·125	—	—	26·4	25	—	—	1085	—	—	—	—	—	—	
—	·25	—	—	22·1	25	—	—	906	—	—	—	—	—	—	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	·5	—	—	17·9	25	·0142	—	736	—	—	—	—	—	—	
—	1·	—	—	14·1	25	—	—	578	—	—	—	—	—	—	
·280	·0625	—	—	75·8[2]	18	—	1212	1288	—	—	—	—	—	—	[3] Berthelot, *Annales de Chimie*, vol. xxiii. p. 49.
·560	·125	—	—	131·3	18	—	1050	1116	—	—	—	—	—	—	
—	·25	—	—	219·7	18	—	879	938	—	—	—	—	—	—	
—	·5	—	—	356·0	18	—	713	758	—	—	—	—	—	—	
·0009	·0002	—	—	185[3]	20	—	—	2331	—	—	—	—	—	—	
·009	·002	—	—	144	20	—	—	1814	—	—	—	—	—	—	
·045	·01	—	—	128	20	—	—	1609	—	—	—	—	—	—	
·090	·02	—	—	119	20	—	—	1506	—	—	—	—	—	—	
·180	·04	—	—	110	20	—	—	1381	—	—	—	—	—	—	

Potassium Oxalate.

Equivalent Gramme Molecule, $\frac{1}{2}(COOK)_2$, 83·13.

—	·5	—	—	373[1]	18	·0214	746	793	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 150.
—	1·	—	—	688	18	·0209	688	730	—	—	—	—	—	—	
—	1·5	—	—	959	18	·0205	640	680	—	—	—	—	—	—	
19·3	—	—	—	—	—	—	—	—	·441[4]	—	—	—	—	—	
—	·0625	—	—	56[2]	18	—	896	953	—	—	—	—	—	—	[2] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
—	·125	—	—	106	18	—	848	901	—	—	—	—	—	—	
—	·25	—	—	198	18	—	792	842	—	—	—	—	—	—	
—	·5	—	—	368	18	—	736	782	—	—	—	—	—	—	[3] Berthelot, *Annales de Chimie*, vol. xxiii. p. 50.
·0055	·00066	—	—	103·9[3]	20	—	—	1186	—	—	—	—	—	—	
·0068	·00082	—	—	103·7	20	—	—	1184	—	—	—	—	—	—	
·0274	·0033	—	—	98·4	20	—	—	1124	—	—	—	—	—	—	
·0548	·0066	—	—	94·9	20	·022	—	1084	—	—	—	—	—	—	[4] Hittorf, *Pogg. Annal.* vol. cvi. p. 371.

Tartaric Acid.

Equivalent Gramme Molecule, $\frac{1}{2}C_2H_2(OH)_2(COOH)_2$, 75.

·00182	·000244	—	—	94·8[1]	25	—	—	2140[3]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 340.
·00365	·000488	—	—	80·3	25	—	—	1813	—	—	—	—	—	—	
·0073	·000976	—	—	67·0	25	—	—	1513	—	—	—	—	—	—	
·0146	·00195	—	—	54·5	25	—	—	1230	—	—	—	—	—	—	
·0292	·0039	—	—	43·1	25	—	—	973	—	—	—	—	—	—	[2] Berthelot, *Annales de Chimie*, vol. xxiii. p. 89.
·0585	·0078	—	—	33·1	25	—	—	747	—	—	—	—	—	—	
·117	·0156	—	—	25·1	25	—	—	567	—	—	—	—	—	—	
·234	·0312	—	—	18·7	25	—	—	422	—	—	—	—	—	—	[3] At 25°.
·468	·0625	1·0016	15	13·7	25	—	—	309	—	—	—	—	—	—	
·934	·125	1·0042	15	9·9	25	—	—	223	—	—	—	—	—	—	
1·86	·25	1·0083	15	7·1	25	—	—	160	—	—	—	—	—	—	
3·69	·5	1·0165	15	5·05	25	—	—	114	—	—	—	—	—	—	
7·26	1·	1·0334	15	3·46	25	—	—	78	—	—	—	—	—	—	
·0015	·0002	—	—	155[2]	17	—	—	2144	—	—	—	—	—	—	
·003	·0004	—	—	135	17	—	—	1867	—	—	—	—	—	—	
·015	·002	—	—	88	17	—	—	1224	—	—	—	—	—	—	
·030	·004	—	—	69·6	17	—	—	963	—	—	—	—	—	—	
·075	·01	—	—	49·4	17	·020	—	683	—	—	—	—	—	—	
·150	·02	—	—	37·0	17	—	—	512	—	—	—	—	—	—	

Benzoic Acid.

Equivalent Gramme Molecule, C_6H_5COOH, 122.

·00298	·000244	—	—	31·7[1]	25	—	—	1433[3]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 343.
·00595	·000488	—	—	24·6	25	—	—	1111	—	—	—	—	—	—	
·0119	·000976	—	—	18·4	25	—	—	832	—	—	—	—	—	—	
·0238	·00195	—	—	13·6	25	—	—	615	—	—	—	—	—	—	
·0475	·0039	—	—	9·95	25	—	—	449	—	—	—	—	—	—	[2] Berthelot, *Annales de Chimie*, vol. xxiii. p. 44.
·095	·0078	—	—	7·20	25	—	—	325	—	—	—	—	—	—	
·190	·0156	—	—	5·20	25	—	—	235	—	—	—	—	—	—	
·00122	·0001	—	—	60·2[2]	17	—	—	833	—	—	—	—	—	—	[3] At 25°.
·0244	·002	—	—	44·4	17	—	—	614	—	—	—	—	—	—	
·061	·005	—	—	29·0	17	—	—	401	—	—	—	—	—	—	
·122	·01	—	—	20·8	17	·020	—	288	—	—	—	—	—	—	

Salicylic Acid.

Equivalent Gramme Molecule, $C_6H_4(OH)COOH$, 138.

			°		°				σ				°		
·0034	·000244	—	—	66·6[1]	25	—	—	3008[3]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 344.
·0068	·000488	—	—	59·9	25	—	—	2704	—	—	—	—	—	—	
·0135	·000976	—	—	51·2	25	—	—	2313	—	—	—	—	—	—	
·027	·00195	—	—	41·8	25	—	—	1886	—	—	—	—	—	—	
·054	·0039	—	—	32·3	25	—	—	1461	—	—	—	—	—	—	[2] Berthelot, *Annales de Chimie*, vol. xxiii. p. 80.
·108	·0078	—	—	25·1	25	—	—	1135	—	—	—	—	—	—	
·216	·0156	—	—	19·1	25	—	—	863	—	—	—	—	—	—	
·0138	·001	—	—	171·2[2]	17	—	—	2367	—	—	—	—	—	—	
·0345	·0025	—	—	128·7	17	—	—	1780	—	—	—	—	—	—	[3] At 25°.
·069	·005	—	—	99·4	17	—	—	1375	—	—	—	—	—	—	
·138	·01	—	—	75·1	17	·020	—	1039	—	—	—	—	—	—	

Metaoxybenzoic Acid.

Equivalent Gramme Molecule, $C_6H_4(OH)COOH$, 138.

·0034	·000244	—	—	34·3[1]	25	—	—	1550[3]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 345.
·0068	·000488	—	—	26·8	25	—	—	1211	—	—	—	—	—	—	
·0135	·000976	—	—	20·3	25	—	—	918	—	—	—	—	—	—	
·027	·00195	—	—	15·2	25	—	—	686	—	—	—	—	—	—	
·054	·0039	—	—	11·2	25	—	—	507	—	—	—	—	—	—	[2] Berthelot, *Annales de Chimie*, vol. xxiii. p. 82.
·108	·0078	—	—	8·24	25	—	—	372	—	—	—	—	—	—	
·216	·0156	—	—	5·99	25	—	—	271	—	—	—	—	—	—	
·432	·0312	—	—	4·31	25	—	—	195	—	—	—	—	—	—	
·0138	·001	—	—	71·9[2]	17	—	—	994	—	—	—	—	—	—	[3] At 25°.
·0345	·0025	—	—	48·1	17	—	—	663	—	—	—	—	—	—	
·069	·005	—	—	35·0	17	—	—	484	—	—	—	—	—	—	
·138	·01	—	—	25·2	17	·020	—	349	—	—	—	—	—	—	

Paroxybenzoic Acid.

Equivalent Gramme Molecule, $C_6H_4(OH)COOH$, 138.

·0034	·000244	—	—	22·8[1]	25	—	—	1029[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 345.
·0068	·000488	—	—	17·2	25	—	—	776	—	—	—	—	—	—	
·0135	·000976	—	—	12·7	25	—	—	573	—	—	—	—	—	—	
·027	·00195	—	—	9·2	25	—	—	416	—	—	—	—	—	—	[2] At 25°.

·054	·0039	—	—	6·65	25	—	—	300	—	—	—	—	—	—	[3] Berthelot, *Annales de Chimie*, vol. xxiii. p. 84.
·108	·0078	—	—	4·77	25	—	—	215	—	—	—	—	—	—	
·216	·0156	—	—	3·38	25	—	—	153	—	—	—	—	—	—	
·432	·0312	—	—	2·39	25	—	—	108	—	—	—	—	—	—	
·0138	·001	—	—	42·6[3]	17	—	—	589	—	—	—	—	—	—	
·0345	·0025	—	—	28·0	17	—	—	387	—	—	—	—	—	—	
·069	·005	—	—	20·0	17	—	—	276	—	—	—	—	—	—	
·138	·01	—	—	14·3	17	·020	—	198	—	—	—	—	—	—	

ORTHONITROBENZOIC ACID.

Equivalent Gramme Molecule, $C_6H_4(NO_2)COOH$, 167·04.

·00405	·000244	—	—	72·6[1]	25	—	—	3280[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 347.
·0081	·000488	—	—	70·9	25	—	—	3203	—	—	—	—	—	—	
·0162	·000976	—	—	67·2	25	—	—	3037	—	—	—	—	—	—	
·0325	·00195	—	—	61·8	25	—	—	2789	—	—	—	—	—	—	
·065	·0039	—	—	54·3	25	—	—	2453	—	—	—	—	—	—	[2] At 25°.
·130	·0078	—	—	45·9	25	—	—	2073	—	—	—	—	—	—	
·260	·0156	—	—	37·4	25	—	—	1688	—	—	—	—	—	—	
·521	·0312	—	—	29·3	25	—	—	1321	—	—	—	—	—	—	

METANITROBENZOIC ACID.

Equivalent Gramme Molecule, $C_6H_4(NO_2)COOH$, 167·04.

·00405	·000244	—	—	53·4[1]	25	—	—	2410[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 347.
·0081	·000488	—	—	44·7	25	—	—	2021	—	—	—	—	—	—	
·0162	·000976	—	—	35·8	25	—	—	1616	—	—	—	—	—	—	
·0325	·00195	—	—	27·7	25	—	—	1250	—	—	—	—	—	—	
·065	·0039	—	—	20·8	25	—	—	934	—	—	—	—	—	—	[2] At 25°.
·130	·0078	—	—	15·3	25	—	—	691	—	—	—	—	—	—	
·260	·0156	—	—	11·2	25	—	—	505	—	—	—	—	—	—	

PARANITROBENZOIC ACID.

Equivalent Gramme Molecule, $C_6H_4(NO_2)COOH$, 167·04.

·00405	·000244	—	—	54·6[1]	25	—	—	2464[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 348.
·0081	·000488	—	—	45·8	25	—	—	2069	—	—	—	—	—	—	
·0162	·000976	—	—	37·1	25	—	—	1676	—	—	—	—	—	—	
·0325	·00195	—	—	28·9	25	—	—	1307	—	—	—	—	—	—	[2] At 25°.

Orthochlorbenzoic Acid.

Equivalent Gramme Molecule, $C_6H_4ClCOOH$, 156·46.

			°		°					°			°		
·0038	·000244	—	—	67·4[1]	25	—	—	3046[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 349.
·0076	·000488	—	—	61·9	25	—	—	2794	—	—	—	—	—	—	
·0152	·000976	—	—	53·8	25	—	—	2431	—	—	—	—	—	—	
·0305	·00195	—	—	44·7	25	—	—	2018	—	—	—	—	—	—	
·061	·0039	—	—	35·5	25	—	—	1605	—	—	—	—	—	—	[2] At 25°.
·122	·0078	—	—	27·6	25	—	—	1246	—	—	—	—	—	—	

Metachlorbenzoic Acid.

Equivalent Gramme Molecule, $C_6H_4ClCOOH$, 156·46.

·0038	·000244	—	—	43·6[1]	25	—	—	1971[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxii. p. 349.
·0076	·000488	—	—	34·9	25	—	—	1577	—	—	—	—	—	—	
·0152	·000976	—	—	20·9	25	—	—	946	—	—	—	—	—	—	
·0305	·00195	—	—	20·4	25	—	—	921	—	—	—	—	—	—	
·061	·0039	—	—	15·1	25	—	—	683	—	—	—	—	—	—	[2] At 25°.

Potassic Hydrate.

Equivalent Gramme Molecule, KHO, 56·13.

·000056	·00001	—	—	—	18	—	747[1]	794	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 196.
·000112	·00002	—	—	—	18	—	845	898	—	—	—	—	—	—	
·000336	·00006	—	—	—	18	—	1474	1567	—	—	—	—	—	—	
·000561	·0001	—	—	—	18	—	1689	1795	—	—	—	—	—	—	
·00112	·0002	—	—	—	18	—	1892	2011	—	—	—	—	—	—	[2] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 353.
·00336	·0006	—	—	—	18	—	2074	2205	—	—	—	—	—	—	
·00561	·001	—	—	—	18	—	2110	2243	—	—	—	—	—	—	
·0112	·002	—	—	—	18	—	2140	2275	—	—	—	—	—	—	
·0336	·006	—	—	—	18	—	2141	2276	—	—	—	—	—	—	[3] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·0561	·01	—	—	—	18	·0194	2124	2258	—	—	—	—	—	—	
·168	·03	—	—	—	18	—	2078	2209	—	—	—	—	—	—	
·280	·05	1·0019	15	—	18	—	2045	2174	—	—	—	—	—	—	
·558	·1	1·0047	15	—	18	—	1986	2111	—	—	—	—	—	—	[4] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
—	·103	—	—	—	—	—	—	—	·742[4]	—	—	—	—	—	
—	·190	—	—	—	—	—	—	—	·730	—	—	—	—	—	
2·743	·5	1·0230	15	—	18	·0188	1841	1957	—	—	—	—	—	—	
—	·804	—	—	—	—	—	—	—	·739	—	—	—	—	—	
5·376	1·	1·0440	15	—	18	·0187	1718	1826	—	—	—	—	—	—	

14·93	3·	1·1274	15	—	18	·0191	1314	1397	—	—	—	—	—	—
23·17	5·	1·2109	15	—	18	·0204	990	1052	—	—	—	—	—	—
39·83	10·	1·4091	15	—	18	·0273	423	450	—	—	—	—	—	—
·0055	·000975	—	—	228·8[2]	25	—	—	2141	—	—	—	—	—	—
·0109	·00195	—	—	231·2	25	—	—	2164	—	—	—	—	—	—
·0219	·00390	—	—	233·1	25	—	—	2181	—	—	—	—	—	—
·0438	·0078	—	—	232·6	25	—	—	2177	—	—	—	—	—	—
·0875	·0156	—	—	230·7	25	—	—	2158	—	—	—	—	—	—
·175	·0312	—	—	228·9	25	—	—	2142	—	—	—	—	—	—
·350	·0625	1·0026	15	225·3	25	—	—	2108	—	—	—	—	—	—
·697	·125	1·0061	15	220·2	25	—	—	2063	—	—	—	—	—	—
1·386	·25	1·0121	15	214·6	25	—	—	2008	—	—	—	—	—	—
2·743	·5	1·0230	15	206·4	25	—	—	1932	—	—	—	—	—	—
·238	·0424	—	—	82·5[3]	18	—	1946	2069	—	—	—	—	—	—
·457	·0816	—	—	158	18	—	1938	2060	—	—	—	—	—	—
·575	·103	1·0049	15	210	18	—	2039	2162	—	—	—	—	—	—
·857	·1537	1·0077	15	292	18	—	1900	2020	—	—	—	—	—	—
1·146	·206	1·0101	15	408	18	—	1980	2105	—	—	—	—	—	—
2·272	·412	1·0191	15	786	18	—	1908	2028	—	—	—	—	—	—
4·467	·825	1·0367	15	1470	18	—	1782	1894	—	—	—	—	—	—

Sodic Hydrate.

Equivalent Gramme Molecule, NaOH, 40·04.

1·954	·5	1·0225	15	817[1]	18	·0194	1634	1737	—	—	—	—	—	—
3·828	1·	1·0441	15	1488	18	·0199	1488	1581	—	—	—	—	—	—
7·366	2·	1·0850	15	2447	18	·0209	1223	1300	—	—	—	—	—	—
10·68	3·	1·1224	15	3020	18	·0221	1007	1070	—	—	—	—	—	—
13·81	4·	1·1569	15	3264	18	·0241	816	867	—	—	—	—	—	—
16·79	5·	1·1896	15	3259	18	·0266	652	693	—	—	—	—	—	—
30·	10·	1·3320	15	1896	18	·0452	190	202	—	—	—	—	—	—
·00385	·000975	—	—	211·6[2]	25	—	—	1980	—	—	—	—	—	—
·0077	·00195	—	—	215·1	25	—	—	2013	—	—	—	—	—	—
·0155	·0039	—	—	216·7	25	—	—	2028	—	—	—	—	—	—
·0311	·0078	—	—	215·2	25	—	—	2011	—	—	—	—	—	—
·0622	·0156	—	—	212·4	25	—	—	1988	—	—	—	—	—	—
·124	·0312	—	—	210·7	25	—	—	1972	—	—	—	—	—	—
·248	·0625	1·0023	15	205·0	25	—	—	1918	—	—	—	—	—	—

[1] Kohlrausch, *Wied. Annal.* vol. vi. p. 150.

[2] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 355.

Sodic Hydrate—*continued.*

Equivalent Gramme Molecule, NaOH, 40·04.

			°		°					°						
—	·108	—	—	—	—	—	—	—	·843[4]	—	—	—	—	—	[3] Lenz, *Mémoire de l'Acad. de St Pétersbourg*, vol. xxvi.
·495	·125	1·0055	15	199·3	25	—	—	1865	—	—	—	—	—	—	
·986	·25	1·0120	15	191·0	25	—	—	1787	—	—	—	—	—	—	
—	·285	—	—	—	—	—	—	—	·800	—	—	—	—	—	
1·954	·5	1·0225	15	181·6	25	—	—	1691	—	—	—	—	—	—	[4] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
—	1·084	—	—	—	—	—	—	—	·827	—	—	—	—	—	
·127	·0319	—	15	56·7[3]	18	—	1777	1889	—	—	—	—	—	—	
·240	·0602	1·0022	15	106	18	—	1760	1871	—	—	—	—	—	—	
·501	·1257	1·0056	15	217	18	—	1722	1830	—	—	—	—	—	—	
·642	·1618	1·0074	15	287	18	—	1771	1883	—	—	—	—	—	—	
1·012	·2564	1·0121	15	424	18	—	1515	1610	—	—	—	—	—	—	
1·274	·3237	1·0150	15	548	18	—	1691	1797	—	—	—	—	—	—	
2·515	·6474	1·0286	15	1022	18	—	1579	1678	—	—	—	—	—	—	
4·893	1·2947	1·0576	15	1805	18	—	1394	1481	—	—	—	—	—	—	

Lithium Hydrate.

Equivalent Gramme Molecule, LiOH, 24·02.

·0023	·000976	—	—	204·4[1]	25	—	—	1913	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 356.
·0047	·00195	—	—	206·3	25	—	—	1931	—	—	—	—	—	—	
·0094	·0039	—	—	206·8	25	—	—	1935	—	—	—	—	—	—	
·0188	·0078	—	—	205·9	25	—	—	1927	—	—	—	—	—	—	
·0375	·0156	—	—	202·2	25	—	—	1892	—	—	—	—	—	—	[2] Kohlrausch, *Wied. Annal.* vol. vi. p. 151.
·075	·0312	—	—	199·6	25	·0194	—	1868	—	—	—	—	—	—	
·150	·0625	—	—	193·8	25	—	—	1814	—	—	—	—	—	—	
·300	·125	—	—	186·5	25	—	—	1745	—	—	—	—	—	—	
—	·25	—	—	179·2	25	—	—	1677	—	—	—	—	—	—	[3] Kuschel, *Wied. Annal.* vol. xiii. p. 289.
—	·201	—	—	—	—	—	—	—	·857[3]	—	—	—	—	—	
—	·402	—	—	—	—	—	—	—	·863	—	—	—	—	—	
—	·5	—	—	694[2]	18	·0191	1388	1475	—	—	—	—	—	—	
—	1·	—	—	1253	18	·0196	1253	1332	—	—	—	—	—	—	
—	1·495	—	—	—	—	—	—	—	·890	—	—	—	—	—	
—	2·	—	—	2108	18	·0202	1054	1120	—	—	—	—	—	—	
—	3·	—	—	2660	18	·0215	887	943	—	—	—	—	—	—	

Barium Hydrate.

Equivalent Gramme Molecule, $\frac{1}{2}Ba(OH)_2$, 85·5.

·0083	·000976	—	—	218·4[1]	25	—	—	2322[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 357.
·0166	·00195	—	—	219·8	25	—	—	2336	—	—	—	—	—	—	
·0332	·0039	—	—	218·7	25	—	—	2325	—	—	—	—	—	—	
·0665	·0078	—	—	215·9	25	—	—	2295	—	—	—	—	—	—	[2] At 25°.
·133	·0156	—	—	210·3	25	—	—	2235	—	—	—	—	—	—	
·266	·0312	—	—	201·0	25	—	—	2137	—	—	—	—	—	—	
·532	·0625	—	—	192·3	25	—	—	2044	—	—	—	—	—	—	
—	·125	—	—	183·9	25	—	—	1955	—	—	—	—	—	—	
—	·25	—	—	174·4	25	—	—	1854	—	—	—	—	—	—	

Strontium Hydrate.

Equivalent Gramme Molecule, $\frac{1}{2}Sr(OH)_2$, 60·75.

·0059	·000976	—	—	209·2[1]	25	—	—	2224[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 357.
·0118	·00195	—	—	212·2	25	—	—	2256	—	—	—	—	—	—	
·0236	·0039	—	—	211·7	25	—	—	2250	—	—	—	—	—	—	
·0472	·0078	—	—	209·0	25	—	—	2222	—	—	—	—	—	—	[2] At 25°.
·0945	·0156	—	—	202·5	25	—	—	2152	—	—	—	—	—	—	
·189	·0312	—	—	196·5	25	—	—	2089	—	—	—	—	—	—	
·378	·0625	—	—	190·1	25	—	—	2021	—	—	—	—	—	—	

Calcium Hydrate.

Equivalent Gramme Molecule, $\frac{1}{2}Ca(OH)_2$, 37.

·0036	·000976	—	—	213·2[1]	25	—	—	2266[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 357.
·0072	·00195	—	—	215·4	25	—	—	2290	—	—	—	—	—	—	
·0144	·0039	—	—	213·4	25	—	—	2268	—	—	—	—	—	—	
·0288	·0078	—	—	209·3	25	—	—	2225	—	—	—	—	—	—	[2] At 25°.
·0575	·0156	—	—	200·2	25	—	—	2128	—	—	—	—	—	—	
·115	·0312	—	—	190·5	25	—	—	2025	—	—	—	—	—	—	

Ammonia.

Equivalent Gramme Molecule, NH_3, 17·04.

·000017	·00001	—	—	—	18	—	560[1]	595	—	—	—	—	—	—	[1] Kohlrausch, *Wied. Annal.* vol. xxvi. p. 197.
·000034	·00002	—	—	—	18	—	700	744	—	—	—	—	—	—	
·000102	·00006	—	—	—	18	—	690	733	—	—	—	—	—	—	

Ammonia—*continued.*

Equivalent Gramme Molecule, NH_3, 17·04.

			°		°					°			°		
·00017	·0001	—	—	—	18	—	610	648	—	—	—	—	—	—	[2] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 358.
·00034	·0002	—	—	—	18	—	500	531	—	—	—	—	—	—	
·00102	·0006	—	—	—	18	—	330	351	—	—	—	—	—	—	
·0017	·001	—	—	—	18	—	260	276	—	—	—	—	—	—	
·0034	·002	—	—	—	18	—	190	202	—	—	—	—	—	—	
·0102	·006	—	—	—	18	—	116	123	—	—	—	—	—	—	[3] At 25°.
·017	·01	—	—	—	18	—	92	98	—	—	—	—	—	—	
·051	·03	—	—	—	18	—	50	53	—	—	—	—	—	—	
·085	·05	—	—	—	18	—	43	46	—	—	—	—	—	—	
·17	·1	—	—	—	18	—	31	33	—	—	—	—	—	—	
·85	·5	—	—	—	18	—	12	12·7	—	—	—	—	—	—	
1·71	1·	·9928	16	—	18	—	8·4	8·9	—	—	—	—	—	—	
5·22	3·	·9776	16	—	18	—	3·3	3·5	—	—	—	—	—	—	
—	5·	—	—	—	18	—	2·4	2·5	—	—	—	—	—	—	
—	10·	—	—	—	18	—	·5	·53	—	—	—	—	—	—	
·00165	·000975	—	—	37·0[2]	25	—	—	393[3]	—	—	—	—	—	—	
·0033	·00195	—	—	25·8	25	—	—	274	—	—	—	—	—	—	
·0066	·0039	—	—	17·9	25	—	—	189	—	—	—	—	—	—	
·0132	·0078	—	—	12·4	25	—	—	132	—	—	—	—	—	—	
·0265	·0156	—	—	8·7	25	—	—	92	—	—	—	—	—	—	
·053	·0312	—	—	6·13	25	—	—	65	—	—	—	—	—	—	
·106	·0625	—	—	4·27	25	—	—	45	—	—	—	—	—	—	
·212	·125	—	—	3·01	25	—	—	32	—	—	—	—	—	—	
·425	·25	—	—	2·10	25	—	—	22	—	—	—	—	—	—	
·85	·5	—	—	1·46	25	—	—	15·5	—	—	—	—	—	—	

Methylamine.

Equivalent Gramme Molecule, CH_3NH_2, 31·04.

·00305	·000976	—	—	108·0[1]	25	—	—	1148[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 360.
·0061	·00195	—	—	84·7	25	—	—	900	—	—	—	—	—	—	
·0122	·0039	—	—	64·8	25	—	—	689	—	—	—	—	—	—	
·0245	·0078	—	—	49·0	25	—	—	521	—	—	—	—	—	—	
·049	·0156	—	—	36·2	25	—	—	385	—	—	—	—	—	—	[2] At 25°.

·098	·0312	—	—	26·4	25	—	—	281	—	—	—	—	—	—	
·195	·0625	—	—	19·1	25	—	—	204	—	—	—	—	—	—	
·39	·125	—	—	13·5	25	—	—	144	—	—	—	—	—	—	
·78	·25	—	—	9·5	25	—	—	101	—	—	—	—	—	—	
—	·5	—	—	6·4	25	—	—	68	—	—	—	—	—	—	

Ethylamine.

Equivalent Gramme Molecule, $C_2H_5NH_2$, 45·04.

·0044	·000976	—	—	112·0[1]	25	—	—	1190[2]	—	—	—	—	—	—	
·0088	·00195	—	—	88·0	25	—	—	936	—	—	—	—	—	—	
·0175	·0039	—	—	66·9	25	—	—	711	—	—	—	—	—	—	
·035	·0078	—	—	50·2	25	—	—	533	—	—	—	—	—	—	
·070	·0156	—	—	36·9	25	—	—	393	—	—	—	—	—	—	
·140	·0312	—	—	26·8	25	—	—	285	—	—	—	—	—	—	
·281	·0625	—	—	19·3	25	—	—	205	—	—	—	—	—	—	
·562	·125	—	—	13·5	25	—	—	144	—	—	—	—	—	—	
—	·25	—	—	9·3	25	—	—	99	—	—	—	—	—	—	
—	·5	—	—	6·1	25	—	—	64	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 360.

[2] At 25°.

Propylamine.

Equivalent Gramme Molecule, $C_3H_7NH_2$, 59·04.

·0042	·000976	—	—	97·7[1]	25	—	—	1038[2]	—	—	—	—	—	—	
·0084	·00195	—	—	77·2	25	—	—	821	—	—	—	—	—	—	
·0169	·0039	—	—	59·2	25	—	—	629	—	—	—	—	—	—	
·0338	·0078	—	—	44·3	25	—	—	471	—	—	—	—	—	—	
·0675	·0156	—	—	32·6	25	—	—	347	—	—	—	—	—	—	
·135	·0312	—	—	23·7	25	—	—	252	—	—	—	—	—	—	
·37	·0625	—	—	16·9	25	—	—	180	—	—	—	—	—	—	
·74	·125	—	—	11·9	25	—	—	127	—	—	—	—	—	—	
—	·25	—	—	8·1	25	—	—	86	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 361.

[2] At 25°.

Isobutylamine.

Equivalent Gramme Molecule, $C_4H_9NH_2$, 73·04.

·0071	·000976	—	—	82·3[1]	25	—	—	875[2]	—	—	—	—	—	—	
·0142	·00195	—	—	64·5	25	—	—	686	—	—	—	—	—	—	
·0285	·0039	—	—	49·2	25	—	—	523	—	—	—	—	—	—	
·057	·0078	—	—	36·6	25	—	—	389	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 361.

[2] At 25°.

Isobutylamine—*continued.*

Equivalent Gramme Molecule, $C_4H_9NH_2$, 73·04.

			°		°				°				°		
·114	·0156	—	—	26·9	25	—	—	286	—	—	—	—	—	—	
·228	·0312	—	—	19·4	25	—	—	207	—	—	—	—	—	—	
·455	·0625	—	—	13·8	25	—	—	147	—	—	—	—	—	—	
·91	·125	—	—	9·6	25	—	—	103	—	—	—	—	—	—	
—	·25	—	—	6·4	25	—	—	69	—	—	—	—	—	—	

Amylamine.

Equivalent Gramme Molecule, $C_5H_{11}NH_2$, 87·04.

·0085	·000976	—	—	97·5[1]	25	—	—	1036[2]	—	—	—	—	—	—	
·017	·00195	—	—	77·4	25	—	—	823	—	—	—	—	—	—	
·034	·0039	—	—	59·9	25	—	—	637	—	—	—	—	—	—	
·068	·0078	—	—	44·4	25	—	—	472	—	—	—	—	—	—	
·136	·0156	—	—	33·2	25	—	—	354	—	—	—	—	—	—	
·272	·0312	—	—	24·2	25	—	—	257	—	—	—	—	—	—	
·544	·0625	—	—	17·2	25	—	—	183	—	—	—	—	—	—	
—	·125	—	—	11·9	25	—	—	127	—	—	—	—	—	—	
—	·25	—	—	7·9	25	—	—	84	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 362.

[2] At 25°.

Dimethylamine.

Equivalent Gramme Molecule, $(CH_3)_2NH$, 45·04.

·0044	·000976	—	—	120·7[1]	25	—	—	1283[2]	—	—	—	—	—	—	
·0088	·00195	—	—	95·7	25	—	—	1017	—	—	—	—	—	—	
·0175	·0039	—	—	73·9	25	—	—	786	—	—	—	—	—	—	
·035	·0078	—	—	55·9	25	—	—	595	—	—	—	—	—	—	
·070	·0156	—	—	41·6	25	—	—	442	—	—	—	—	—	—	
·140	·0312	—	—	30·4	25	—	—	323	—	—	—	—	—	—	
·281	·0625	—	—	21·8	25	—	—	232	—	—	—	—	—	—	
·562	·125	—	—	15·4	25	—	—	164	—	—	—	—	—	—	
—	·25	—	—	10·6	25	—	—	113	—	—	—	—	—	—	
—	·5	—	—	6·9	25	—	—	73	—	—	—	—	—	—	

[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 363.

[2] At 25°.

Diethylamine.

Equivalent Gramme Molecule, $(C_2H_5)_2NH$, 73·04.

·0071	·000976	—	—	130·3[1]	25	—	—	1382[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 363.
·0142	·00195	—	—	108·4	25	—	—	1152	—	—	—	—	—	—	
·0285	·0039	—	—	85·9	25	—	—	913	—	—	—	—	—	—	
·057	·0078	—	—	65·8	25	—	—	699	—	—	—	—	—	—	[2] At 25°.
·114	·0156	—	—	49·4	25	—	—	525	—	—	—	—	—	—	
·228	·0312	—	—	36·1	25	—	—	384	—	—	—	—	—	—	
·455	·0625	—	—	26·0	25	—	—	277	—	—	—	—	—	—	
·910	·125	—	—	18·2	25	—	—	193	—	—	—	—	—	—	
—	·25	—	—	12·3	25	—	—	131	—	—	—	—	—	—	

Trimethylamine.

Equivalent Gramme Molecule, $(CH_3)_3N$, 59·04.

·0058	·000976	—	—	56·81	25	—	—	604[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 364.
·0116	·00195	—	—	42·8	25	—	—	455	—	—	—	—	—	—	
·0231	·0039	—	—	32·2	25	—	—	342	—	—	—	—	—	—	
·0462	·0078	—	—	23·7	25	—	—	252	—	—	—	—	—	—	[2] At 25°.
·0925	·0156	—	—	17·3	25	—	—	183	—	—	—	—	—	—	
·185	·0312	—	—	12·5	25	—	—	132	—	—	—	—	—	—	
·370	·0625	—	—	8·9	25	—	—	94	—	—	—	—	—	—	
·740	·125	—	—	6·2	25	—	—	66	—	—	—	—	—	—	
—	·25	—	—	4·2	25	—	—	44	—	—	—	—	—	—	
—	·5	—	—	2·63	25	—	—	28	—	—	—	—	—	—	

Triethylamine.

Equivalent Gramme Molecule, $(C_2H_5)_3N$, 101·04.

·0099	·000976	—	—	111·6[1]	25	—	—	1186[2]	—	—	—	—	—	—	[1] Ostwald, *Journ. für Chemie*, vol. xxxiii. p. 364.
·0198	·00195	—	—	87·6	25	—	—	931	—	—	—	—	—	—	
·0395	·0039	—	—	66·6	25	—	—	708	—	—	—	—	—	—	
·079	·0078	—	—	49·7	25	—	—	528	—	—	—	—	—	—	[2] At 25°.
·158	·0156	—	—	36·4	25	—	—	387	—	—	—	—	—	—	
·315	·0312	—	—	26·1	25	—	—	277	—	—	—	—	—	—	
·630	·0625	—	—	18·5	25	—	—	196	—	—	—	—	—	—	
—	·125	—	—	12·6	25	—	—	134	—	—	—	—	—	—	
—	·25	—	—	8·2	25	—	—	88	—	—	—	—	—	—	
—	·5	—	—	4·8	25	—	—	51	—	—	—	—	—	—	

INDEX.

The numbers refer to the pages. Authors' names are printed in small capitals. The electrochemical properties of aqueous solutions of the substances of which the names appear in italics will be found tabulated in the Appendix.

ABEGG and NERNST, theory of freezing point determinations, 153
Absolute electric charge on ions, 189
Absolute ionic velocities, 214; table of, 223
Absolute scale of temperature, 15.
Absorption coefficients, 85, 87
Absorptiometer (Fig. 33), 84, 85
Accelerating influence of acids, 337
Accumulators or secondary cells, 263; electromotive force, 265; origin, 181
Acetic acid, 453; abnormal vapour pressure, 129; freezing point of solutions in, 156; ionic mobilities, 215, 218; ionization, 321; ionization constant, 341
Acetate of silver, solubility of, 93
Acetone, conductivity of solutions in, 331
Acids, accelerating influence, 337; electrical conductivities, 204, 337, 357
Action, secondary electrolytic, 194
Additive properties of solutions, 332
Adiabatic relations of ideal gas, 7
ADIE, absolute value of osmotic pressure, 120
Affinity or avidity, coefficient, 205, 336, 342; measurement, 336; residual, 173
AITKEN, supersaturation, 43
Alcohol, ionization of solutions in, 322, 331; vapour pressures, 72, 74, 403
ALEXEJEFF, mutual solubility of liquids, 88
Alkalis, electrolytic decomposition of, 178
ALKEMADE, VAN RIJN, VAN, ζ curves, 26, 63
Allotropic solids (Fig. 12), 45
Alloys, 59; eutectic, 60; mixed crystals, 69; freezing point, 60, 160; microscopic study, 60, 62, 68; rate of cooling, 68; structure (Figs. 43, 44), 144; copper and tin, 71; gold aluminium, 61, 62; fusion curve (Fig. 20), 62; silver copper, 59, 60; fusion curve (Fig. 19), 60
Alternating currents, used in measurement of electrolytic conductivity, 199
Aluminium chloride, 420; *sulphate*, 445
Amalgams, in capillary electrometers and galvanic cells, 285; in concentration cells, 244; in dropping electrodes, 281; vapour pressure of, 141
Ammonia, 471; ionization, 216, 322; solubility, 86
Ammonium bichromate, 450; *chloride*, 412; *chromate*, 450; *iodide*, 424; *nitrate*, 428; *sulphate*, 438
Amylamine, 474
Anhydrous solutes (Fig. 13), 50, 51
Animal electricity, 176
Anion, definition of, 180
Anode, definition of, 180
ARCHIBALD, equivalent conductivities at 0°, 325; freezing point, 153
ARMSTRONG, H. E., hydrate theory of solution, 170
ARMSTRONG, E. F., Report by, 403
ARRHENIUS, chemical activity, 336; coefficient of ionization, 322; electrolytic dissociation, 317; diffusion of electrolytes, 380; freezing points, 153; heat of neutralization, 356; heat of ionization, 355; ionic fluidity, 224; maxima conductivities, 357; osmotic pressure of electrolytes, 317
ASTON and DUTOIT, equivalent conductivities, 331
Available energy, *see* Energy
Avidity, measurement, 336; table of relative, 337

Ayrton and Perry, potential differences, 268

Bancroft, "the Phase Rule," 77, 402; potential differences, 388
Barium chloride, 415; *hydrate*, 471; *nitrate*, 432
Barnes, freezing points, 153; equivalent conductivity at 0°, 325
Battery, *see* Cell
Beckmann, boiling points, 137; freezing point determinations, apparatus for (Fig. 45), 155; freezing points of concentrated solutions, 161; molecular weights in solution, 140; vapour pressures, 132, 133
Beetz, electrolytes, resistance of, 198; conductivity of supersaturated solutions, 80
Bein, electrolytic transport numbers, 210
Beketoff, precipitation of metals by hydrogen, 386
Bemmelen, van, gelation, 394
Bender, properties of solutions, 333
Benzine, freezing points of, solutions in, 156
Benzoic acid, 465
Berkeley, Earl of, growth of crystals, 81; time required for saturation, 90
Berthelot, occlusion, 82
Berthelot and Jungfleisch, solubility of succinic acid, 93
Berzelius, electrochemical theory, 191
Berzelius and Hisinger, electrolytic decomposition of salt solutions, 178
Bindel, supersaturated solutions, 80
Blagden, freezing points of solutions, 153
Boiling points, 135, 331; measurement of, by Beckmann, 137; Buchanan, 138; Regnault, 138; Wade, 140
Boltzmann, laws of osmotic pressure, 169
Bottomley, potential differences, 271
Boundary of two solutions, 219, 376, 382
Bouty, measurement of electrolytic conductivity, 198
Boyle's Law, 7
Bredig, specific ionic mobility, 229, 230
Bredig, Cohen and Van 't Hoff, transition cells, 261
Bredig, Noyes and Ostwald, concentrated solutions, 162
Brompropionic acid, 459
Brown, J., temperature coefficient of fused salt cells, 237; mercury dropping electrodes, 280; potential differences, 271
Brühl, ionizing power of water, 364
Bruni and Padoa, solid solutions, 403
Brunner, precipitation of metals by hydrogen, 386
Buchanan, J. Y., boiling point of solutions, 138, 139; cryohydric point, lowering of, 146; freezing of sea water, 145; freezing point of sodium chloride solutions, 142; structure of ice, 145
Bunsen, absorption coefficient, 85; confirmation of Henry's law, 86; determination of solubility, 84
Burch, action of capillary electrometer, 283; electrometer as condenser, 282
Buscemi, temperature coefficient of fused salt cells, 237
Butyric acid, 460

Cadmium bromide, 422; *chloride*, 419; *iodide*, 424; *nitrate*, 433; *sulphate*, 443
Cailletet, evolution of hydrogen by metals, 386
Calcium chloride, 416; *hydrate*, 471; *nitrate*, 432
Calorie, definition of, 1
Cane sugar, inversion of, 337; freezing point of solutions, 147
Capacity for heat of solutions, 171, 335
Capacity, specific inductive, of solvents, 362
Capillary action, electro-, 282; electrometer, 282
Carlisle and Nicholson, early experiments on electrolysis, 177
Carnallite, deposition of, 404
Carnot's engine, 12
Carrara, dissociation of water, 363; equivalent conductivities in pyridine, 331
Cathode, definition of, 180
Cation, definition of, 180
Cells, galvanic: amalgam, 285; bichromate, 182; chemical, 255; Clark's standard, 184, 235, 261; Daniell's, 182, 233; effect of pressure, 239; electromotive force, 232, 235, 236, 285, 288, 382, 383; fused salt, 237; Grove's, 235, 237; irreversible, 235, 262; liquid, 382; mercury, reversible heat of, 238; reduction and oxidation, 258; reversible 234, 235, 237; secondary, 263; Smee's 182; temperature coefficient of, 237; transition, 258; Weston's, 261
Cells, concentration: calomel, 250; von Helmholtz's theory, 242; hydrogen, 242; silver chloride, 249; silver nitrate, 245, 248; different electrodes, 242; different solutions, 245; double concentration, 250; effect of low concentration, 253; ionization in, 255; migration in, 250; table of electromotive forces, 250
Cells, osmotic (Fig. 36), 96, 118, 168
Cells, resistance (Figs. 48 to 51), 201
Change of volume and osmotic pressure, 111

Charpy, alloys, 59; microscopic study of, 61
Chemical affinity, *see* Affinity
Chemical combination, theory of solution, 169
Chemical constitution and mobility of ions, 229
Chemical potential, 25, 34
Chloric acid, 434
Christy, contact potentials, 300
Clark, Latimer, standard cell, 184, 235, 261
Clausius, on electrolysis, 205; latent heat equation, 38
Coagulation of colloidal solutions, 45, 395
Cobalt sulphate, 445
Cohen, hydrated solids, 53; transition point, 259
Cohen, van 't Hoff and Bredig, transition cells, 261
Collins, Richards and Heimrod, electrochemical equivalent of silver, 185
Colloid, definition of, 371
Colloidal solutions, coagulation of, 45, 395; nature of, 400; separation from crystalloids, 388
Colour of salt solutions, 334
Combination, chemical, theory of osmotic pressure, 169
Comey, A. M., Dictionary of Chemical Solubilities, 93
Commutator, revolving, 201; tuning-fork, 301
Complete cycles, 6
Complex cycles, 18
Complex ions, 226, 322, 331
Complex, molecular, theory of solutions, 173
Components, definition of, 35; one component, 39; two components, 48; consolute, 48; two liquid, 58; two volatile, 71; three, 76
Compound, definition of, 48
Concentrated solutions, equation for, 162; freezing point of, 160; freezing point and osmotic pressure, 150; vapour pressure of, 126
Concentration cells, 241; *see* Cells, concentration
Concentration curves, 55; *see* Curves
Concentration, influence of, on equivalent conductivity, 223
Concentration, ionic, 340, 346, 351, 365
Conductivity, electrolytic, 197, 408; additive nature of, 207; equivalent, 202, 408; connexion with osmotic pressures, freezing points and vapour pressures, 160, 316; influence of concentration (Fig. 12), 202, 203, 223, 322; of liquid films, 230; in various solvents, 322, 330, 362; measurement of, 198, 325; of mixed solutions, 88; temperature coefficient of, 202, 408; of supersaturated solutions, 80; of water, 193, 358
Consolute components, 48
Consolute solid solutions, 63
Contact electricity, 267 *et seq.*
Contact potentials, 300; table of, 285
Contact of two solutions, 219, 376, 382
Contraction on formation, 171
Convergence temperature, 154
Co-ordinates, generalized, 18
Copper chloride, 419; *sulphate*, 443
Copper refining, 310
Corpuscles, or negative ions, 191, 274
Crompton, heat of neutralization, 352
Cruikshank, experiments on electrolytes, 178
Cryohydrates, 49
Cryohydric point, 142; lowering of, 146
Crystalline structure of alloys, 68, 71, 144; of ice, 47, 144
Crystallization, 44, 81, 171, 392
Crystalloid, definition of, 371; separation of, 380
Crystals, mixed, 62, 69, 403
Crystals, surface energy of, 45, 81
Cupric chloride, 419; *sulphate*, 443
Current, alternating, used in measuring electrolytic conductivity, 199
Curves, concentration or solubility (Figs. 16 to 32, 34, 35, 52, 64, 66), 55 to 79, 89, 91, 328, 404; conductivity (Figs. 52, 64), 203, 328; electrocapillary (Fig. 61), 288; fusion and solidification (Figs. 16 to 25, 40, 64), 55 to 70, 125, 328; ionization (Fig. 64), 328; Phase Rule (Figs. 8 to 15, 31, 40), 39 to 54, 76, 125; vapour pressure (Figs. 26 to 30, 40, 41), 72 to 75, 125, 136; ζ (Figs. 7, 21 to 24), 26, 64 to 67
Cyanacetic acid, ionization constant of, 342
Cycles, complete, 6; complex, 18
Czapski, temperature coefficient of cells, 237

Dalton's law, 48
Daniell, cell, 182, 233; nature of ions, 192
Davy, Sir Humphry, electrolysis, 178; electrolytic decomposition of alkalis, 178; polarization, 181
Decomposition, electrolytic, 178; of water, 178, 306, 307
Decomposition voltages, 301; tables, 302, 308
De Coppet, cryohydric temperatures, 143; freezing point of solutions, 153; of supersaturated solutions, 80

Density of solutions, 170, 333, 408; of supersaturated solutions, 80
Depression of the freezing point, 126; *see* also Freezing Points
Des Coudres, mercury concentration cell, 244
Deville and Troost, occlusion, 82
De Vries, isotonic solutions, 119
Dewar, occlusion, 82
Diagrams of apparatus, absorptiometer (Fig. 33), 85; boiling point (Fig. 42), 139; capillary electrometer (Fig. 60), 282; electrolytic conductivity (Figs. 47 to 51), 200 to 202; freezing point (Fig. 45), 155; ionic migration (Figs. 54, 55, 56), 210, 217, 221; normal electrode (Fig. 62), 295; osmotic cell (Fig. 36), 96; polarization (Fig. 63), 303
Dialysis, 388
Dichloracetic acid, 456
Dieterici, vapour pressure of sulphuric acid, 265
Diethylamine, 475
Diffusion, 369; constant of, 369; absolute value, 371; tables, 372, 373; of electrolytes, 376; experiments on, 370; through membranes, 388; and osmotic pressure, 374; theory, 369, 374, 376
Diffusivity or diffusion constant, 369
Dilatometer, 46
Dilution, effect of, 169; heat of, and osmotic pressure, 111; law of, 341, 343, 344, 350
Dimethylamine, 474
Dissipation of energy, principle of, 110
Dissociation, electrolytic, theory of, 206, 312; and chemical activity, 335; heat of, 354; and osmotic pressure, 159, 316; of water, 358, 362
Dissociation, hydrolytic, 364
Dissolution, heat of, 112, 171; table, 117
Divariant systems, 36
Dolezalek, theory of accumulators, 264, 265
Donders and Hamburger, temperature and osmotic pressure, 118, 119
Donnan, colloid solutions, 402; Hall effect in electrolytes, 385
Double concentration cells, 250
Double salts, 92; electrolysis, 195; deposition, 403
Dropping electrodes, 278, 281
Duhem, theory of colloids, 394
Dutoit and Aston, conductivities of solutions in acetone, 331; properties of solvents, 364

Eckard, dialysis, 389
Edler and Oberbeck, potential differences, 388
Efflorescence of crystals, 54, 58
Electric charge of ions, 188, 189
Electric endosmose, 292
Electricity, animal, 176; contact, 267
Electro-capillary action, 282, 294
Electro-chemical equivalents, 184; table of, 187
Electro-chemical properties, table of, 407
Electro-chemical series, 177, 296, 298, 299
Electrodes, definition of, 180; of different concentration, 242; dropping, 278, 281; platinum, preparation of, 199; tapping, 198
Electrolysis, 176, et seq.; of gases, 187
Electrolytes, additive properties, 332; coagulative properties, 395; conductivity of, 197; conductivity of and depression of freezing point, 160; diffusion of, 376; equilibrium between, 346; measurement of conductivity of, 198; potential differences between, 381; solution pressure of, 256; thermal properties of, 352
Electrolytic conductivity, 197, 408
Electrolytic separations, 301
Electrolytic solution pressure, 274, 280, 297, 385
Electrometer, capillary, 282
Electromotive force, of galvanic cells, 236, 238, 240, 243, 247, 257, 259, 381
Electromotive series of metals, 177, 296, 298, 299
Electrons, theory of, 191, 274
Electroplating, 178, 194, 307
Emden, vapour pressure of solutions, 132
Endosmose, electric, 292
Energy, available or free, 28, 29; applications to chemical change, 339; coordination of physical science, 165; dilution of solutions, 169; electro-capillary action, 284; electromotive force, 235; heat of ionization, 354; latent heat, 29; osmotic pressure, 103, 113, 165
Energy, conservation of, 1; internal, 19; surface, 43, 81, 402
Engel and Etard, influence of temperature on solubility, 91
Engine, Carnot's reversible, 12
Entropy, 20
Equilibrium, 10, 32, 205, 225, 339; conditions of, 25; electrolytic, 205, 225, 339, 346; false, 11, 37; labile, 42; of phases, 33, 68, 78; in saturated solutions, 78
Equivalent conductivity, tables of, 408
Equivalent conductivity, curves showing (Fig. 52), 202, 203; influence of concentration, 223; limiting value, 332;

measurement at 0°, 325; in various solvents, 321, 330, 362
Equivalent, electro-chemical, 184; table of, 187
Erman, voltaic pile, 178
Erskine Murray, contact electricity, 272
Etard and Engel, influence of temperature on solubility, 91
Ethereal solutions, lowering of vapour pressure in, 132
Ethyl alcohol, ionization in, 322, 330
Ethylamine, 473
Ethyl-sulphuric acid, 446
Ewan, T., freezing point of concentrated solutions, 150
Ewing and Rosenhain, structure of alloys (Fig. 44), 144
Eutectic alloys, 60, 144
Evolution of gases in polarization, 305
Exner, mercury-dropping electrodes, 280; single potential differences, 278
Exner and Tuma, single potential differences, 278
Expansion, thermal, 171; of salt solutions, 333
Eyk van, equilibrium of solid and liquid phases, 68
Eykman, freezing points, 150, 161

False equilibrium, 11, 37
Faraday, early experiments on electrolysis, 179; laws of electrolysis, 182; polarization, 181; vapour pressures, 132
Faraday's laws, 182, 184, 332; in fused salts, 187; in gases, 187
Favre, occlusion, 82
Ferric chloride, 421; equilibrium of phases (Fig. 17), 56; efflorescence of crystals, 54; hydrolysis, 366
Ferrous chloride, 420
Ferrous sulphate, 444
Fick, diffusion, 369, 371
Films, gaseous, 82, 269, 271; liquid, conductivity of, 230
FitzGerald, osmotic pressure and surface tension, 100, 103
FitzGerald and Trouton, conductivity of electrolytes, 204
Fitzpatrick, electrolytic conductivity, 201, 330; *tables of electro-chemical properties*, 211, 407
Fluidity, ionic, 224, 356
Fluidity of solutions, 409; *temperature coefficient of*, 409
Forces, generalized, 19
Formic acid, 452; freezing points of solutions in, 156
Formic acid series, mobility of ions, 230
Fourier, conduction of heat, 369
Fractionation, 75, 403
Free energy, *see* Energy
Free surface of volatile liquid, 98
Freezing points, 40, 126, 141, 153, 317; of alloys, 59, 62, 69, 144, 160; depression of the, 123, 126, 142, 147, 149, 150, 156, 160, 162, 317, 320, 322, 328, 330, 400; diagrams (Figs. 16 to 25, 40, 64), 55 to 70, 125, 328; experimental methods (Fig. 45), 153, 155, 158; non-aqueous solutions, 156, 321, 330; connexion with electrolytic conductivity, 159, 316 to 332; with osmotic pressure, 126, 147, 152; with vapour pressure, 122, 125
Friction coefficients, ionic, tables of, 379
Fuchs, electromotive force of polarization, 303
Fused salt cells, temperature coefficient of, 237
Fusion curves, *see* Freezing Point Diagrams

Galvani, origin of electrolysis, 176; animal electricity, 176
Galvanic circuit, distribution of potential in (Figs. 58, 59), 275
Galvanism, identity with electricity, 178
Gamgee, colloids and crystalloids, 401
Gas, adiabatic relations of an ideal, 17; electrolysis, 187, 189; polarization, 305; solubility in liquids, 84, 130; solubility in mixed solutions, 87; solubility in salt solutions, 87; solubility in solids, 81
Gas, battery, Grove's, 305
Gaseous film, 82, 269, 271
Gaseous pressure, identity with osmotic pressure, 104, 120, 166
Gelation, 394
Generalized co-ordinates, 18; forces, 19
Gibbs, chemical potential, 25, 34; electromotive force of reversible cells, 235; growth of crystals, 45, 81; latent heat equation, 38; phase rule, 35; theory of osmotics, 109; transition cells, 258; surface energy, 81, 402
Gilbault, effect of pressure on electromotive force, 240
Gill, reversible heat of cell, 238
Gladstone, colour of salt solutions, 335
Gockel, temperature coefficient of electromotive force, 237
Goodwin, double concentration cells, 252
Gore, surface of contact of two solutions, 219
Gorski and Laszozynski, equivalent conductivities, 331
Graham, colloids, 391, 396; diffusion, 370, 372; occlusion, 82
Gram-molecule, definition of, 4
Griffiths, freezing points of dilute solu-

tions, 158, 321; mechanical equivalent of heat, 1; molecular lowering of freezing point, 147
Groshaus, properties of solutions, 333
Grotthus, electrolytic chain, 180; electrolytic decomposition, 179
Grove, cell, 235; gas cell, 305
Guldberg and Waage, the mass law, 205, 340
Guthe and Patterson, electro-chemical equivalent of silver, 185
Guthrie, alloys, 59; cryohydrates, 49; equilibria of mixtures of salts, 76

Hall effect in electrolytes, 384
Hall and Kahlenberg, equivalent conductivity at 0°, 325
Hamburger and Donders, influence of temperature on osmotic pressure, 118
Hardy, coagulation, 398; gelation, 394; gels, 393
Hautefeuille and Troost, occlusion, 82
Heat, latent, equation, 29, 30, 37, 125
Heat of dilution, calculation of freezing point from, 170; and osmotic pressure, 111; of sulphuric acid, 266
Heat of formation, determination, 238; table, 117
Heat of ionization, 354
Heat of precipitation, 117
Heat of reaction, 237
Heat of solution and solubility, 90, 115; and osmotic pressure, 112; of supersaturated solutions, 80; table of, 117
Heat, reversible, of cell, 237
Heat, specific, of supersaturated solutions, 80
Heidenhain and Meyer, absorptiometer (Fig. 32), 84
Heim, electrical conductivity of supersaturated solutions, 80
Heimrod, Collins and Richards, electrochemical equivalent of silver, 185
Helmholtz, von, electro-capillary action, 283; electric endosmose, 293; electromotive force, 235; free energy, 28; migration in concentration cells, 250; osmotics, 109; potential differences, 279
Henderson and Stroud, measurement of electrolytic conductivity, 197
Henry's law, 85; confirmed by Bunsen, 86
Hess, law of thermo-neutrality, 352
Heycock and Neville, on alloys, 59 et seq.; copper and tin (Fig. 19), 71; depression of freezing point, 160; gold and aluminium (Fig. 30), 62, and (Fig. 43), 144; microscopic investigations, 59, 61, 62, 68, 71, 144 (Fig. 43); osmotic pressure, 244
Heydweiler and Kolhrausch, conductivity of pure water, 193, 358
Hisinger and Berzelius, electrolysis of salt solutions, 178
Hissink, equilibrium of solid and liquid phases, 68
Hittorf, chemical activity and conductivity, 336; complex ions, 226; electrochemical series, 300; electrodes of concentration cells, 254; electrolysis of double salts, 195; migration of ions, 208, 210, 383; secondary action in electroplating, 194
Hoff, van 't, diffusion and osmotic pressure, 376; dilution law, 343; influence of pressure on solubility, 90; latent heat equation, 38; molecular depression of freezing point, 149; osmotic pressure, absolute value of, 103, 107; osmotic theory, 172; solubility of mixtures, 403; table of heats of solution or precipitation, 117
Hoff, van 't, Cohen and Bredig, transition cells, 261
Hoitsema, solid solutions, 83
Hoitsema and Roozeboom, occlusion, 82
Holborn and Kohlrausch, equivalent and electrochemical weights, 186; transport numbers, 211
Hopfgartner, transport numbers, 210
Horn and Morse, semi-permeable membranes, 406
Horsford, resistance of electrolytes, 198
Hosking and Lyle, ionic viscosity, 406
Houllevigne and Osmond, electrolysis of salts of iron, 196
Hydrated solids, 53
Hydrates, crystallization of, 171; formation of, 57; isolation of, 171
Hydrate theory of solution, 170
Hydriodic acid, 422
Hydrobromic acid, 421
Hydrochloric acid, 410; solubility, 75, 84, 87
Hydrocyanic acid, 451; solutions in, 406
Hydroferrocyanic acid, 451
Hydrofluoric acid, 425
Hydrogels, 393
Hydrogen, concentration cell, 242
Hydrolysis, 364
Hydrolytic dissociation, 364
Hydrosols, 393

Ice, arctic, 145; crystalline varieties of, 47; structure of, 47, 144;
Index, refractive, 171; and boundary of solutions, 121
Indicator diagram, 14
Internal energy, 19
Inversion of cane sugar, 337

Inversion point, 41, 55, 259, 262
Iodides, mixture of, freezing point curve (Fig. 25), 69, 70
Iodopropionic acid, 460
Ionic concentration, 245, 253, 300, 308, 317, 326, 340, 348, 365, 397
Ionic fluidity, 224, 356, 379, 406
Ionic migration, theory of, 208, 213, 383
Ionic viscosity, 224, 356, 379, 406
Ions, charge on, 189; complex, 226, 322, 331; as condensation nuclei, 43; dissociation, in electrolysis, 206; fluidity, 224; migration, 207, 210; mobility, 211 to 226, 229, 230; nature of, 191
Ionization, 225, 316, 325, 328, 337, 341, 354, 358, 362, 406; heat of, 354; in various solvents, 330, 331, 362, 406
Ionization of dilute solutions at 0°, 321, 325, 328
Irreversible cells, 262
Isobutylamine, 473
Isobutyric acid, 461
Isohydric solutions, 346
Isomorphous salts, 92
Isotonic coefficients, 120
Isotonic solutions, 119

Jahn, heats of formation, 238; reactions in electrolysis, 194; reversible heat in cells, 237, 238; temperature coefficient of cells, 237
Jones, H. C., freezing points, 153; ionization at 0°, 328
Joule, measurement of thermal equivalent of work, 1
Jungfleisch and Berthelot, solubility of succinic acid, 93

Kahlenberg, abnormal molecular weights in solution, 322, 332; chemical reactions, 339; freezing point data, 330
Kahlenberg and Hall, equivalent conductivity at 0°, 325
Kahlenberg and Schlundt, ionizing power of solvents, 363, 406
Kelvin, Lord (Sir Wm Thomson), capillary action, 100; dropping electrodes, 278; electromotive force and heat of reaction, 237; latent heat equation, 38; principle of classification, 110; similarity of laws for gases and solutions, 169; thermo-electricity, 272
Kistiakowsky, electrolytic transport numbers, 210
Kohlrausch, F., alternating currents, 199; boundaries of solutions, 220; conductivity of solutions, 80, 199, 202; conductivity of water, 193; electrolysis of platinum chloride, 196; equivalent conductivity of solutions, 202; ionic friction coefficients, 379; ionic mobility or velocity, 211; Ohm's law in electrolysis, 177, 204; use of telephone, 199
Kohlrausch, F. and W., electro-chemical equivalent of silver, 185
Kohlrausch and Heydweiler, conductivity of pure water, 193, 358
Kohlrausch and Holborn, electrochemical and equivalent weights, 186; tables of electrolytic transport numbers, 211
Konowaloff, vapour pressure of miscible liquids (Figs. 26 to 30), 72 to 75
Krapiwin and Zelinsky, conductivity of solutions in alcohol, 330
Kümmel, electrolytic transport numbers, 210
Kuschel, electrolytic transport numbers, 210

Laar van, electrocapillary phenomena, 287
Labile equilibrium, 42
Lactic acid, 462
Lamb, theory of electric endosmose, 294
Larmor, diffusion, 374, 384; electrocapillary action, 283; migration of ions, 209; osmotic theory, 105, 109; thermo-electricity, 272
Laszozynski, conductivity of solutions in acetone, 331
Laszozynski and Gorski, conductivity of solutions in pyridine, 331
Latent heat, and available energy, 29, 30; le Chatelier's theorem, 37, 38; and boiling point, 136; and freezing point, 142; osmotic pressure and heat of solution, 114; freezing point and vapour pressure, 125
Law of available or free energy, 28, 29
Law of diffusion, Fick's, 371
Law, dilution, 341, 344
Law of thermoneutrality, 352
Law, Henry's, 85
Law, the mass, 339
Law, Ohm's, 197, 204
Law, Volta's, 276
Laws, Faraday's, of electrolysis, 182
Laws of osmotic pressure, 103, 120, 166
Laws of thermodynamics, 1, 2
Laws of vapour pressure for mixed vapours, 71, 406
Le Blanc, decomposition point, 308; evolution of gases, 305; polarization, 301, 303, 304; single potential differences, 387
Lead nitrate, 434
Le Chatelier, alloys, 59; latent heat, 38
Lehfeldt, electrolytic solution pressure, 299; electromotive force of concentration cell, 247

Lehmann, nature of amorphous bodies, 47
Lenz, electrolytic transport numbers, 210
Lincoln, ionization in various solvents, 331
Linder and Picton, coagulative power of electrolytes, 395, 396, 399; nature of colloidal solution, 400
Lippmann, capillary electrometer, 282, 284
Liquid cells, 382
Liquid, free surface of a volatile, 98
Liquids, miscibility of, 88
Liquids, mixed, laws of vapour pressure for, 71, 403; mixed, solubility in, 93; separation of, by fractionation, 74, 403; solubility of, in liquids, 88; undercooled, 42, 392, 402
Liquidus curve, 66, 69
Lithium butyrate, 461; *carbonate*, 449; *chlorate*, 435; *chloride*, 414; *formate*, 453; *hydrate*, 470; *iodide*, 424; *isobutyrate*, 462; *nitrate*, 430; *perchlorate*, 436; *propionate*, 459; *sulphate*, 440; *trichloracetate*, 458
Lodge, Sir Oliver, measurement of ionic velocity, 216; potential differences, 270
Loeb and Nernst, electrolytic transport numbers, 210
Longden, conductivity of metallic films, 231
Loomis, freezing points of solutions, 153, 321, 328
Lyle and Hosking, conductivity and fluidity of solutions, 406

MacGregor, freezing point data, 330; measurement of electrolytic conductivity, 201; properties of dilute solutions, 333
Magnesium chloride, 417; *nitrate*, 433; *sulphate*, 440
Magnetic rotation of solutions, 171, 335
Manganese chloride, 420
Marignac, thermal capacity of salt solutions, 335
Mass law of chemical action, 205, 339
Masson, Orme, ionic velocities, 220; table, 221
Membranes, diffusion through, 388; perfect semipermeable, 102; semipermeable, 95, 406
Mendeléeff, hydrates in solutions, 170
Mercury concentration cells, 243
Metachlorbenzoic acid, 468
Metals, electromotive series, 177, 296, 298, 299
Meta-nitrobenzoic acid, 467
Meta-oxybenzoic acid, 466
Methyl alcohol, ionization in, 331
Methylamine, 472
Methyl sulphuric acid, 445
Meyer, G., electromotive force of concentration cell, 246; mercury dropping electrodes, 281
Meyer and Heidenhain, absorptiometer (Fig. 33), 84
Microscopic study of alloys, 68, 71, 144
Migration of ions, 207, 383
Migration constants, 210, 212, 222, 408
Migration, elimination of, in concentration cells, 250
Migration, ionic, theory of, 208, 383
Miscibility of liquids, 88
Mixture, definition, 48; solubility, 92 (Fig. 66), 403, 404
Mobility, ionic, 214 to 226
Molecular bombardment, theory of, 167
Molecular complexes, 170
Molecular weight in solution, 140, 158, 316, 324
Monckman and J. J. Thomson, filtration of permanganate, 98
Mond, Ramsay and Shields, occlusion, 82, 83
Monobromacetic acid, 457
Monochloracetic acid, 455
Monovariant systems, 36
Morgan, ionization of double cyanides, 255
Morse and Horn, semipermeable membranes, 406
Moser, theory of concentration cell, 242

Nernst, chemical cells, 255; concentration cells, 248, 250, 382; diffusion, 281, 374, 376; electrolytic solution pressure, 274, 280, 385; equilibrium in solutions, 347; galvanic cells, 240; ionizing power of solvents, 361; liquid cells, 252, 382; metallic and electrolytic conductivity, 184; reversible heat of mercury cells, 238; solubility in mixed liquids, 93; solubility of silver acetate, 93
Nernst and Abegg, theory of freezing point determination, 153
Nernst and Loeb, electrolytic transport numbers, 210
Neumann, single potential differences, 296, 387
Neville, alloys forming mixed crystals, 69; freezing and melting point curves, 66
Neville and Heycock, *see* Heycock and Neville
Nicholson and Carlisle, early experiments on electrolysis, 177
Nickel chloride, 420; *sulphate*, 444
Nicol, additive properties of salt solutions, 334
Nitric acid, 426

Nitrobenzene, solutions in, freezing points of, 157
Non-electrolytes, freezing points, 153, 319; osmotic pressures, 104, 120; vapour pressures, 129
Non-variant systems, 35
Novak, ionization of water, 362
Noyes, electrolytic transport numbers, 228
Noyes, Bredig and Oswald, freezing points of concentrated solutions, 162

Oberbeck, polarization, 304
Occlusion, 82
Oettingen, von, contact potentials, 300
Ohm's law in electrolytes, 197, 204
Organic cells and osmotic pressure, 118, 389
Osmond, alloys, 59, 61
Osmond and Houllevigne, electrolysis of salts of iron, 196
Osmotic pressure, 95, et seq., absolute value of, 103, 106, 109, 120, 166, 316 to 332; and boiling point, 122; corpuscular, 274; and diffusion, 374; effect of concentration on, 117; effect of temperature on, 118; of electrolytes, 116, 120, 157, 159, 175, 316 to 332; experimental measurement, 95, 117, 406; and freezing point, 126, 152; and gaseous pressure, 103, 106, 109, 120, 166; and heat of solution, 112; of metallic solutions, 141, 160, 244; and organic cells, 118, 389; and surface tension, 97, 100, 390; theoretical laws of, 103, 120, 166, 316 to 332; and vapour pressure, 91, 98, 123, 127
Osmotics, theory of, 103 to 112, 120, 166, 175, 316 to 332
Ostwald, additive properties of solutions, 333; acidity, measurement of, 336; colour of solutions, 334; conditions for production of current, 234; concentration cells, 253; dilution law, 341, 344; dissociation of water, 360; heat of ionization, 357; ionic mobility, 229, 230; mass law, 340; solubility, 84, 85, 92; volume change of salt solutions, 334
Ostwald, Bredig and Noyes, concentrated solutions, 162
Ostwald and Walker, measurement of vapour pressure, 133
Oxidation and reduction cells, 258
Oxygen, valency and ionizing power, 364

Padoa and Bruni, solid solutions, 403
Palmaer, electrolytic solution pressure, 281
Paschen, mercury dropping electrodes, 281
Patterson and Guthe, electro-chemical equivalent of silver, 185
Pellat, electro-capillary action, 284
Pellat and Potier, electro-chemical equivalent of silver, 185
Peltier effect, 238, 273
Perkin, magnetic rotation in solutions, 335
Perry and Ayrton, metallic potential differences, 268
Pfeffer, osmotic pressure, 95, 117, 120
Phase Rule, 32 et seq., 394, 402, 433
Phase, definition of, 33
Phases, equilibrium of, 33
Phenol and water, concentration curve (Fig. 18), 58
Pickering, concentrated solutions, 163; densities of solutions, 170; freezing points, 153; hydrate theory of solution, 170, 171; permeability of membranes, 96, 172
Pile, Volta's, 176
Planck, diffusion, 281, 374, 384; electrolytic dissociation, 317; galvanic cells, 240; liquid cells, 383
Platinum thermometry, 59, 147, 158
Poincaré, L., temperature coefficient of fused salt cells, 237
Poiseuille, laws of, 293
Polarization, 181, 300, 303, 305; elimination of 182, 198, 199; and contact electricity, 267
Polymerisation, gaseous, 161; at high concentrations, 161; in solutions, 364; in solvents of benzene series, 159
Ponsot, convergence temperature, 154; freezing points of solutions, 161, 162, 328
Potassium acetate, 454; *bichromate*, 450; *bromide*, 422; *butyrate*, 460; *carbonate*, 448; *chlorate*, 434; *chloride*, 411; *chromate*, 450; *cyanide*, 451; *fluoride*, 426; *formate*, 452; *hydrate*, 468; *iodide*, 423; *isobutyrate*, 462; *lactate*, 463; *nitrate*, 427; *oxalate*, 464; *perchlorate*, 436; *propionate*, 458; *sulphate*, 437; *trichloracetate*, 457
Potassium chloride, ionization, 321, 327, 328
Potential, chemical, 25, 34; graphical method of representing (Figs. 7, 21 to 24), 26, 64 to 67
Potential differences, 267 et seq., 381; between electrolytes, 242 et seq., 381; in galvanic circuit (Figs. 58, 59), 275; single, 275, 294; tables of, 285, 296; summation of, 268, 276
Potential, thermodynamic, 23, 25, 64
Potier and Pellat, electro-chemical equivalent of silver, 185

Poynting, depression of freezing point, 126; osmotic and gaseous pressure, 173; theory of osmotic pressure, 174
Pressure, osmotic, *see* osmotic pressure
Pressure, effect on electromotive force of cells, 239; effect on metals, 41; effect on solubility, 83, 85, 90; vapour, *see* vapour pressure
Pyridine, equivalent conductivity of solutions in, 331, 332

Quincke, coagulation, 399; electric endosmose, 292

Ramsay, vapour pressure of amalgams, 141, 244
Ramsay, Mond and Shields, occlusion, 82, 83
Rankine, latent heat equation, 38
Raoult, freezing points, 147, 153, 156, 161, 162, 328; polarization, 301; vapour pressures, 129, 132
Raoult and Recoura, vapour pressure of acetic acid, 129
Rayleigh, Lord, osmotic pressure, 106, 110; distillation, 403
Rayleigh, Lord, and Mrs Henry Sidgwick, electro-chemical equivalent of silver, 185
Rays, Röntgen, charge on ions produced by, 189
Recoura and Raoult, vapour pressure of acetic acid, 129
Reduction cells, 258
Reed, C. J., accumulators, 263
Refining, copper, 310
Refractive index of solutions, 171, 335; used to determine boundary of solutions, 221
Regnault, measurement of boiling point, 138
Reicher, transition point of sulphur, 46
Reinders, equilibrium of solid and liquid phases, 68
Reinold and Rücker, conductivity of liquid films, 230
Residual affinity, 173
Resistance of electrolytes, 197 et seq.; *see* Conductivity
Reversible engines, 12
Reversible processes, 8
Richards, Collins and Heimrod, electro-chemical equivalent of silver, 185
Rijn, van Alkemade, van, ζ curves, 26, 63
Ritter, action of accumulator, 181; electromotive series of metals, 177
Roberts-Austen, Sir William, gold-aluminium alloy, 61
Roberts-Austen and Stansfield, alloys, 59, 68
Röntgen rays, charge on ions produced by, 189
Roozeboom, allotropic solid (Fig. 12), 46, 47; alloys, 59; equilibrium of hydrates, 57; liquidus and solidus curves, 66; mixtures of iodides (Fig. 25), 69, 70; theory of solid solutions, 63, 68
Roozeboom and Hoitsema, occlusion, 82
Roscoe, distillation of nitric and hydrochloric acids, 75
Roscoe and Schorlemmer, Text-book of Chemistry, 93
Rosenhain and Ewing, structure of alloys (Fig. 44), 145
Rotation, magnetic, of solutions, 171, 335
Rothmund, electrocapillary action, 285
Rowland, mechanical equivalent of heat, 1
Rücker and Reinold, conductivity of liquid films, 230
Rudolphi, dilution law, 343
Rüdorff, freezing points of solutions, 153; solubility of mixtures, 92
Rule, the Phase, 32 et seq., 394, 402, 403
Rutherford, velocity of gaseous ions, 189

Sack, conductivity of copper sulphate, 357
Salicylic acid, 466
Salt deposits, oceanic, 403
Salts, double, 92; electrolysis of, 195
Salts, isomorphous, 92
Salts and water, equilibrium of, 50 et seq., 403
Sand, electrolysis of mixed solutions, 399
Sandbanks, formation of, 401
Saturated solutions, 49 et seq., 78 et seq., 112, 143, 403
Saturation, time required for, 90
Scheffer, diffusion, 372, 380
Schlundt, complex ions, 226; transport numbers, 332
Schlundt and Kahlenberg, ionizing power of solvents, 363, 406
Schorlemmer and Roscoe, Text-book of Chemistry, 93
Schulze, coagulative power of electrolytes, 395, 399
Sea-water, deposition of salts from, 405
Secondary action, 192, 194
Secondary cells, 263
Selenic acid, 446
Semi-permeable membranes, 95, 102, 168, 172, 406; perfect, 102
Series of metals, electromotive, 177, 268, 296, 298, 299
Setschenoff, absorption coefficient, 87
Shaw, W. N., electric endosmose, 195, 294; electro-chemical equivalent of copper, 186
Sheldon and Downing, ionic velocity, 217

Shields, hydrolysis, 366
Shields, Ramsay, and Mond, occlusion, 82, 83
Sidgwick, Mrs Henry, and Lord Rayleigh, electro-chemical equivalent of silver, 185
Silver, electro-chemical equivalent of, 184, 185
Silver acetate, solubility of, 93
Silver nitrate, 430; *sulphate*, 440
Single potential differences, 267 to 292, 294
Skinner, electrolysis of solutions in pyridine, 332
Smale, temperature coefficient of Groves' gas cell, 237
Smee, galvanic cell, 182
Smith, S. W. J., electro-capillary action, 283 (Fig. 61), 288; mercury-dropping electrodes, 281
Sodium acetate, 455; *butyrate*, 461; *carbonate*, 449; *chloride*, 413; *ethyl sulphate*, 446; *formate*, 452; *hydrate*, 469; *iodide*, 424; *isobutyrate*, 462; *lactate*, 463; *methyl sulphate*, 445; *nitrate*, 429; *perchlorate*, 436; *propionate*, 459; *selenate*, 447; *sulphate*, 439; *trichloracetate*, 457
Sodium sulphate, Phase Rule diagram (Fig. 15), 54; solubility curves (Figs. 16, 32), 55, 79
Solidifying point, *see* Freezing point
Solid solutions, 62 to 71, 83, 403
Solids, allotropic, 45; amorphous, 47, 392; hydrated, 53
Solids, solubility in liquids, 89, 90
Solidus curve, 66, 69
Solubility, 27, 48, 55, 78; curves (Figs. 16 to 25, 32, 34, 35, 66), 55 to 70, 79, 89, 91, 404; of gases, 81, 84, 85, 87; of liquids, 88, 92; of solids, 89, 90; tables of, 93, 94
Solute, definition of, 49; anhydrous, 50; hydrated, 53
Solution, 48, 77, 165; heat of, 112; table of heats of, 117; theories of, 165
Solvent, 49, 361, 406; specific inductive capacity, 362, 406
Soret, temperature, diffusion and osmotic pressure, 376
Spiers, contact electricity, 271
Spring, effect of pressure on metals, 41
Stansfield and Roberts-Austen, alloys, 59, 68
Stassfurt, salt deposits, 403
Stead, alloys, 59, 68
Steele, complex ions, 226, 228; ionic velocities, 221
Stefan, theory of diffusion, 372
Streintz, accumulators, 264
Strontium chloride, 415; *hydrate*, 471; *nitrate*, 431
Stroud and Henderson, measurement of electrolytic resistance, 199
Structure of ice, alloys, etc., 143
Succinic acid, solubility of, 93
Sulphur, allotropic forms (Fig. 12), 45
Sulphur dioxide, solubility of, 86
Sulphuric acid, 437; densities of, 170; heat of dilution, 266
Sulphurous acid, 446
Supersaturated solutions, properties of, 80
Supersaturation, 43, 44, 80
Surface energy or surface tension, 43, 44, 80, 287; and potential difference, 288; osmotic pressure, 97, 100, 390
Surfusion, 42, 45, 80, 155, 392
Systems, divariant, 36; monovariant, 36; nonvariant, 35; one component, 39; two component, 49

Tables, accelerating powers, 338; avidities, 337, 338; boiling points, 137, 331; conductivities of acids, 338; contact potentials, 285; cryohydric temperatures, 143; decomposition voltage, 302, 308; diffusion constants, 372, 373; *electro-chemical properties*, 407; electrolytic solution pressure, 298; electromotive force of accumulators, 266; amalgam cells, 285, concentration cells, 250, 252, liquid cells, 382, 383, mercury cells, 290; equivalent conductivities at 0°, 326, 327; equivalent weights and electro-chemical equivalents, 187; freezing points, 149, 156, aqueous solutions of alcohol, 163, cane sugar, 163, electrolytes, 319, 320, 328, 330; non-aqueous solutions in acetic acid, benzene, formic acid, 156, nitrobenzene 157; heat of ionization, 355, 358; heat of neutralization, 356; heat of precipitation or solution, 117; hydrolytic dissociation, 366; ionic friction coefficients, 379; ionic mobilities, 211, 212, 215, 218, 221, 222, 223; ionization constants, 242; ionization of barium chloride, 330, potassium chloride, 328, of solutions in alcohols, 331; migration constants or transport numbers, 212, 222, 408; potential differences, 296; reversible heat of cells, 238; solubility, 93, 94; transport numbers or migration constants, 212, 222, 408; vapour pressures, 132, 133, 134, 137, 331
Tammann, alloys, freezing point of, 160; amorphous solids, 47; crystalline varieties of ice, 47; crystallization, 44; osmotic pressure, 119, 120; pressure and evolution of hydrogen, 386; vapour pressures, 132, 134
Tartaric acid, 465

Taylor, A. E., potential differences, 388
Telephone, used as indicator, 199
Temperature, absolute scale of, 15; coefficient of cells, 237; *coefficient of conductivity*, 408; *coefficient of fluidity*, 409; convergence or equilibrium, 154
Tereschin, specific inductive capacity of solvents, 362
Theory of chemical combination, 169; of direct molecular bombardment, 167; dissociation, hydrate, of solution, 170; of osmotics, 109
Theories of solution, 165
Thermal properties of electrolytes, 333, 335, 352
Thermodynamics, elements of, 1 to 31; laws of, 1, 2
Thermodynamic potential, 23, 25
Thermo-electricity, 272
Thermometry, platinum, 59, 147, 158
Thermo-neutrality, law of, 352
Thomsen, affinity, 336; heat of dilution of sulphuric acid, 266; heat of neutralization, 352
Thomson, James, latent heat equation, 38
Thomson, J. J., charge on ions, 189; corpuscles, 191; effect of pressure on cells, 240; electrolysis of gases, 187; ionizing power of solvents, 361
Thomson, J. J., and Monckman, filtration of potassium permanganate, 98
Thomson, Sir William, *see* Kelvin, Lord
Three component systems, 76
Tilden, solution and chemical action, 172
Tin, solutions in, lowering of freezing point, 160
Townsend, J. S., charge on ions, 190
Transition cells, 258
Transition points 41, 55, 259 (Fig. 57), 261, 262
Transport numbers, 207, 210, 212, 408
Traube, preparation of semi-permeable membranes, 95
Triangular diagram (Fig. 31), 76
Trichloracetic acid, 456
Triethylamine, 475
Trimethylamine, 475
Troost and Deville, occlusion, 82
Troost and Hautefeuille, occlusion, 82
Trouton and FitzGerald, conductivity of electrolytes, 204
Tuma and Exner, single potential differences, 278

Valson, specific gravity of salt solutions, 333
Vapour pressure, abnormal, 129, 134; of amalgams, 141; calculation of, 130; of concentrated solutions, 126; curves for, water and alcohol (Fig. 27), 74, 403, water and formic acid (Fig. 30), 75, water and isobutyl alcohol (Fig. 25), 72, water and methyl alcohol (Fig. 28), 74, water and propyl alcohol (Fig. 26), 74; measurement, 132; ethereal solutions, 132; and freezing points, 122; mixed solutions, 71, 403; and osmotic pressure, 98, 127; tables, 132, 133, 134, 137, 331
Vapour, supersaturated, 42
Velocity of the ions, 179, 188, 189, 208 to 230, 312, 376, 379; absolute, 214; measurement of, 216, 217; tables of, 215, 218, 221, 222, 223
Viscosity of solutions, 335, 409; ionic, 224, 356
Völlmer, conductivities in alcohol, 330, 331
Voigtländer, diffusion, 372, 375
Volatile components, 88
Volatile liquid, free surface of, 98
Volta, contact electricity, 267; early experiments on electrolysis, 176
Volta's law, summation of potential differences, 268, 276
Volta's pile, 176, 178
Voltage decomposition, 181, 301, 308 to 311
Voltameter, silver, 184
Volume, change of, and osmotic pressure, 111; of solutions, 333, 336

Waage and Guldberg, the mass law, 205, 340
Waals, van der, equation of state for gases, 161
Wade, E. B. H., measurement of boiling points, 140
Walker, J., vapour pressures, 132; hydrolysis, 365
Walker and Ostwald, measurement of vapour pressures, 133
Warburg, mercury-dropping electrodes, 280; surface tension and electromotive force, 291
Water, conductivity of, 193, 203, 358, 362; decomposition of, in electrolysis, 178, 193, 306; ionization, 193, 203, 358, 362; preparation of pure, 193, 358; sea, freezing of, 143
Watts, Dictionary of Chemistry, 93
Weber, C. L., specific ionic velocity of copper ions, 216
Weber, H., boundaries of solutions, 220
Weber, H. F., diffusion, 371
Weights, equivalent and electro-chemical, 187; molecular, determination of, in solution, 140, 158; abnormal, 108, 159, 322, 332

WERNER, molecular weight of pyridine, 332
Weston cell, transition point, 261
WEYPRECHT, freezing of sea-water, 145
WHETHAM, W. C. D., coagulative power of electrolytes, 396; complex ions, 226; conductivity, 195, 201, 204, 325; hydrolysis, 367; ionization power of solvents, 362; mobile equilibrium in electrolytes, 225; preparation of platinum electrodes, 200; specific ionic velocities, 217
WIEDEMANN, electrolytic conductivity, 198; endosmose, 292
WIJS, dissociation of water, 360
WILDERMANN, freezing points, 153
WILLIAMSON, theory of chemical change, 206
WILSON, C. T. R., charge on ions, 189; supersaturation and condensation of water vapour, 43
WOELFER, boiling points of solutions in alcohol, 331
WOLLASTON, galvanism and electricity, 178
WOOD, R. W., equivalent conductivity, 325
Work and energy, 3
WÜLLNER, vapour pressures, 132

ζ curves (Figs. 7, 21, 22, 23, 24), 26, 64, 67
ZELINSKY and KRAPIWIN, equivalent conductivities in alcohol, 330
ZENGELIS, electrodes of concentration cells, 254
Zinc chloride, 418; *sulphate*, 441

LIBRARY OF THE UNIVERSITY OF CALIFORNIA

CAMBRIDGE: PRINTED BY J. AND C. F. CLAY, AT THE UNIVERSITY PRESS.

THIS BOOK IS DUE ON THE LAST DATE STAMPED BELOW

AN INITIAL FINE OF 25 CENTS

WILL BE ASSESSED FOR FAILURE TO RETURN THIS BOOK ON THE DATE DUE. THE PENALTY WILL INCREASE TO 50 CENTS ON THE FOURTH DAY AND TO $1.00 ON THE SEVENTH DAY OVERDUE.

OCT 17 1945

LD 21–100*m*-12,'43 (8796s)

YC 21413
U. C. BERKELEY LIBRARIES
C061311370